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Comments and suggestions are welcome.

Profile of the Petroleum Refining Industry in California

California Industries of the Future Program

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Executive Summary

The U.S. Department of Energy (DOE) Office of Industrial Technologies (OIT) established the Industries of the Future (IOF) program to increase energy efficiency, reduce waste production and to improve competitiveness, currently focusing on nine sectors. The IOF is a partnership strategy involving industry, the research community and the government, working together to identify technology needs, promote industrial partnerships and implement joint measures with all partners involved.

The State Industries of the Future (SIOF) program delivers the accomplishments of the national Industries of the Future strategy to the local level, to expand the technology opportunities to a larger number of partners and reach smaller businesses and manufacturers that were not initially involved in the IOF effort. The state programs bring together industry, academia, and state agencies to address the important issues confronting industry in the state. These public-private coalitions facilitate industry solutions locally and enhance economic development. California has started a State Industries of the Future effort, in collaboration with the U.S. Department of Energy.

The California Energy Commission (CEC) is leading the SIOF program in California, as part of many other programs to improve the energy efficiency and performance of industries in California. The California State IOF program aims to build a network of participants from industry, academia and government in four selected industrial sectors as a basis for the development of a strategic partnership for industrial energy efficient technology in the state. As part of this effort the SIOF program will develop roadmaps for technology development for the selected sectors. On the basis of the roadmap, the program will develop successful projects with co-funding from state and federal government, and promote industry-specific energy-efficiency. In California the IOF effort focuses on four industries: petroleum refining, chemical processing, food processing and electronics. This report aims to provide background information for the development of a research and development roadmap for the Californian petroleum refining industry.

Refineries are the largest energy using industry in California, and the most energy intensive industry in the United States. Petroleum refining industries have evolved from relatively simple distillation-based plants to highly complex and integrated distillation and conversion processes. In fact, the petroleum refining industry of today looks more like the chemical industry. Refineries are facing many challenges, e.g. increased fuel quality, heavier crudes and changing product mix, increasing and more volatile energy prices, need to reduce air pollutant emissions, increased pressure on profitability, as well as increased safety demands. These challenges will affect the industry and technology choice profoundly. In this report we have discussed the historical development of the petroleum refining industry in the U.S. and California. The analysis showed that the Californian refining industry is the leader in many of the identified challenges to the national industry.

The U.S. petroleum processes almost 25% of the world's annual crude oil production. The U.S. petroleum refining industry consumes over 3.2 Quads of primary energy, mainly in the form of refinery by-products (e.g. refinery gas, coke), natural gas and electricity. California has the third largest refining industry in the nation, after Texas and Louisiana. The Californian petroleum industry represents approximately 12% of the nation's industry, expressed in crude intake capacity. In California 8 companies operate 14 refineries, with concentrations in the San Francisco Bay area and Los Angeles. The industry in California produces a distinctly different mix of products when compared to the nation's average, which is reflected in the increased demand for lighter products (e.g. gasoline) and cleaner products. This difference is reflected in the processes used by the industry in California, as well as in the energy intensity. There is no public data available on the total energy consumption of petroleum refineries in California. We estimate the primary energy consumption at 495 TBtu.

On the long-term the refinery of the future will be distinctly different from today's. In the report we outlined major technology development areas, and which are summarized in Table 7.

Table 7. Major technology development directions for the petroleum refining industry.

Technology Area	Technology Examples
Process Control	Neural networks, knowledge based systems
Process Optimization and Integration	Analytical tools, site integration
Energy Recovery	Hydrogen recovery and integration, flare gas recovery
Catalysts	Higher selectivity, increased lifetime
Reactor Design	Process intensification, membranes, reactive distillation, dividing-wall column
Biotechnology	Biodesulfurization, bio-feedtsocks
Combustion Technology	Low NOx burners, high-efficiency burners
Utilities	Membranes, low-maintenance pumps
Power Generation	Advanced cogeneration, Gasification (IGCC), power recovery

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1. Introduction

The U.S. Department of Energy (DOE) Office of Industrial Technologies (OIT) established the Industries of the Future (IOF) program to increase energy efficiency, reduce waste production and to improve competitiveness, currently focusing on nine sectors. The IOF is a partnership strategy involving industry, the research community and the government, working together to identify technology needs, promote industrial partnerships and implement joint measures with all partners involved.

The State Industries of the Future (SIOF) program delivers the accomplishments of the national Industries of the Future strategy to the local level, to expand the technology opportunities to a larger number of partners and reach smaller businesses and manufacturers that were not initially involved in the IOF effort. The state programs bring together industry, academia, and state agencies to address the important issues confronting industry in the state. These public-private coalitions facilitate industry solutions locally and enhance economic development. California has started a State Industries of the Future effort, in collaboration with the U.S. Department of Energy.

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An important element of the SIOF-program is the preparation of R&D roadmaps for each of the selected industries. The roadmap will help to identify priority needs for the participating industries to meet its energy challenges. The roadmap effort builds on the roadmaps developed by DOE, and on the conditions specific for the industry in California. Key to the successful preparation of a roadmap in the selected industries is the development of a profile of the industry. The profile provides a basis for the participants in the roadmap-effort, especially as the structure of the industries in California may be different than in the nation. The sector profiles describe the current economic and energy situation of these industries in California, processes and energy uses, as well as the potential future developments in each industry. The profiles are an integral part of the roadmap, to help working group partners to evaluate their industry's R&D needs for their industry in California.

The California SIOF-effort focuses on four important industries, that combined consume a large part of the energy in the state. The four focus industries are: chemicals, petroleum refining, food, and electronics industries. In this report we focus on the profile of the petroleum refining.

Oil production in California goes back to the beginning of the history as a state. Industrial production of oil from the La Brea tar pits started as early as 1856, and the first refining operations started in 1861. Today, the petroleum refining industry in California is concentrated in two areas: the Los Angeles basin (including Bakersfield) and San Francisco Bay. The industry is an important economic factor in these areas, providing nearly 10,000 jobs directly, and a multitude of indirect employment. Value of shipments in 1997 (the latest year for which Census data was available for California) was just over $19 Billion, or 5% of all manufacturing in California. A variety of companies operate 14 refineries in California. It is the single largest energy-consuming industry in California. Energy is key in the conversion of crude oil to clean refined petroleum products. Increased demand for light oil products, efforts to reduce sulfur content in gasoline, and the replacement of MTBE challenge the industry in California. As most refineries are near urban areas, continued public pressure on environmental performance of the refineries leads to increased interest in pollution prevention. Reducing energy consumption through development and implementation of innovative technologies is key for the development of a sustainable oil industry in California.

In this report we start with a description of the petroleum refining industry in the United States and California. This is followed by a description of the major processes used, as well as the distribution of the processes in the U.S. and California refineries. We discuss the Californian refineries in more detail, as the structure of the Californian refining industry is distinctly different from the nation due to the higher demand of lighter and low-sulfur products. In Chapter 4 we assess the energy consumption and energy intensity of the Californian petroleum refining industry. Based on this analysis, in Chapter 5 we discuss technology developments that can contribute to further improving the energy efficiency in refineries, especially with a focus on the situation in California.

2. The Petroleum Refining Industry

We start with a description of the U.S. petroleum refining industry, followed by a description of the industry in California. This will help to put the Californian developments in a broader perspective, and to distinguish the developments specific for California.

2.1 The U.S. Petroleum Refining Industry

The U.S. has the world's largest refining capacity, processing just less than a quarter of all crude oil in the world. Although the major products of the petroleum-refining sector are transportation fuels, its products are also used in other energy applications and as feedstock for the chemical industries.

The petroleum refining sector has grown over the past 50 years by about 2%/year on average. Until the second oil price shock refining capacity grew rapidly, but production already started to levy off in the mid 1970's. This was a period where the industry started to re-organize. It was not until after the mid-1980's that refining capacity started to grow again. Since 1985, the industry has been growing at a somewhat slower rate of 1.4%/year.
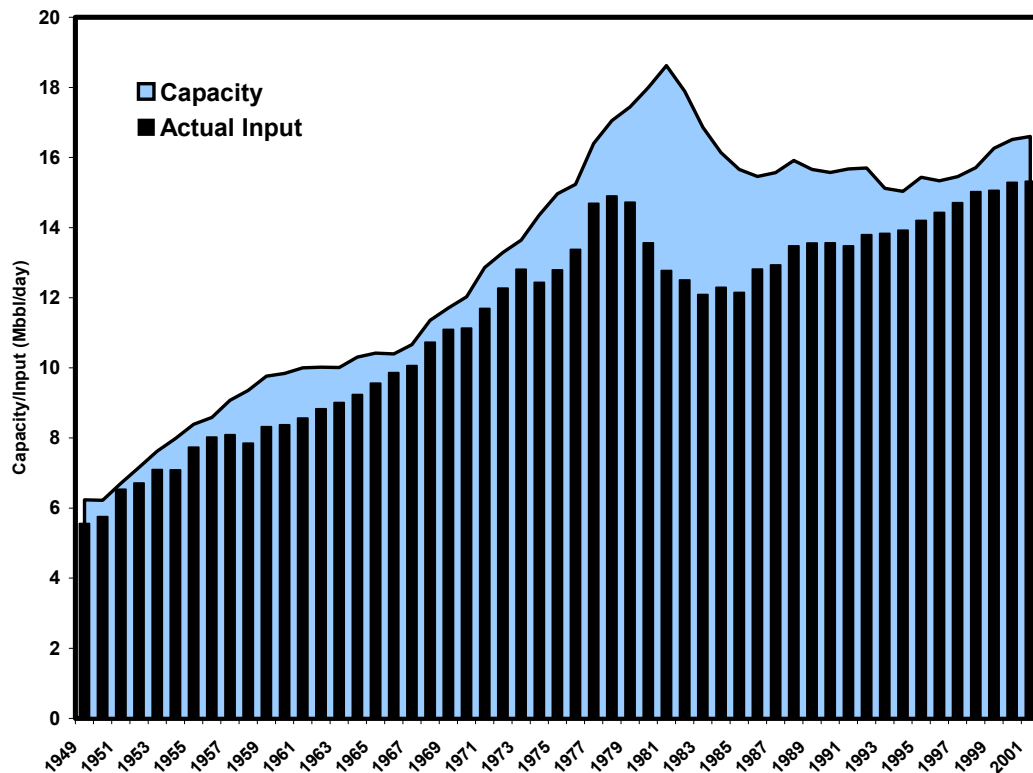

Figure 1. Capacity and actual crude intake of the U.S. petroleum refining industry between 1949 and 2001, expressed in Million barrels/day of crude oil intake. Source: Energy Information Administration.

Figure 1 shows the developments in installed capacity (expressed as crude intake capacity) and actual crude intake in the U.S. Refining industry since 1949. Figure 1 shows that capacity utilization has been pretty steady, with exception for the period between the two oil price shocks. Following the first oil price shock, federal legislation favoring domestic production and refining subsidized the construction and operation of many small refineries (US DOE-OIT, 1998). As shown this had led to a reduced capacity utilization. Figure 2 shows the development of the number of refineries in the United States.
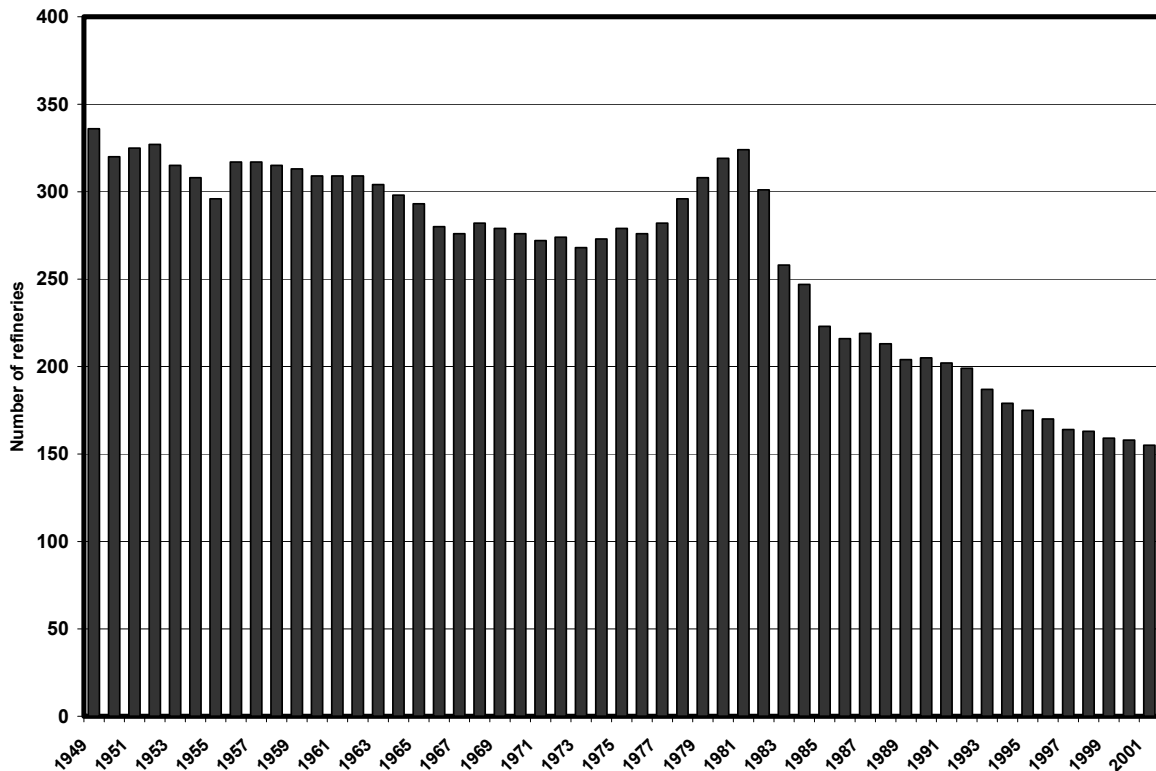

Figure 2. Operating refineries in the United States. Source: Energy Information Administration.

Figure 2 clearly demonstrates the increasing number of refineries after the first oil price shocks in the 1970's. The small refineries only distill products, and are most often inefficient and less flexible operations, only producing a small number of products. Increasing demand for lighter refinery products, and changes in federal energy policy, have led to a reduction in the number of refineries, while increasing capacity utilization (see Figure 1).

These market dynamics will also lead to a further concentration of the refinery industry into high capacity plants operating at higher efficiencies. Since 1990 the number of refineries has declined from 205 (in 1990) to 147 in 2002. The current refineries have a higher capacity utilization and are generally more complex, with an emphasis on converting technology. This trend will continue to increase the ability to process a wider

range of crudes, produce an increasing share of lighter petroleum products, and the need to produce cleaner burning fuels to meet environmental regulations (i.e. reduction of sulfur content). Appendix A provides a list of operating refineries in the United States in January 2002.

Petroleum refineries can be found in 32 states, but the industry is heavily concentrated in a few states due to (historic) resource location and easy access to imported supplies (i.e. close to harbors). Hence, the largest number of refineries can be found on the Gulf coast, followed by California, followed by Illinois, New Jersey, Pennsylvania and Washington. Some of the smallest producing states have only very small refineries operated by independent operators. These small refineries produce only a very small mix of products, and are ultimately not expected to be able to compete in the developing oil market. Figure 3 depicts refining capacity by state (expressed as share of total capacity crude intake) in 2002.
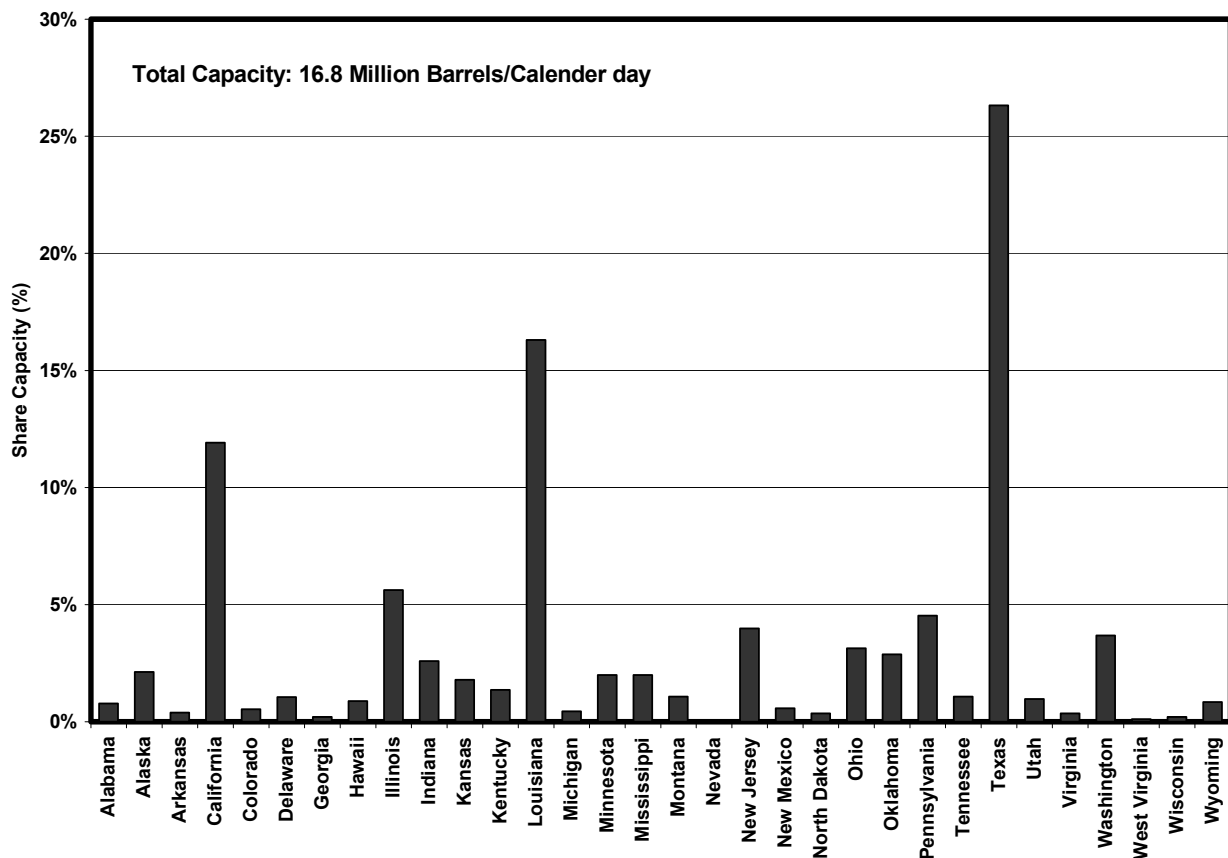
Figure 3. Refining capacity by state as share of total U.S. refining capacity in 2002. Capacity is expressed as capacity for crude intake. Source: Energy Information Administration.

In the U.S. 72 companies operate refineries. Although there are a relatively large number of independent companies in the US refining industry, the majority of the refining capacity is operated by a small number of multi-national or national oil processing

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companies. The largest companies are: ExxonMobil (11% of crude capacity), Philips 66 (10%), BP (9%), ChevronTexaco (6%), Valero (5%), Marathon Ashland (6%) and Motiva (5%), which combined represent 52% of CDU capacity. Each of these companies operates a number of refineries in different states. Figure 4 depicts companies operating over 0.5% of CDU capacity in the U.S.
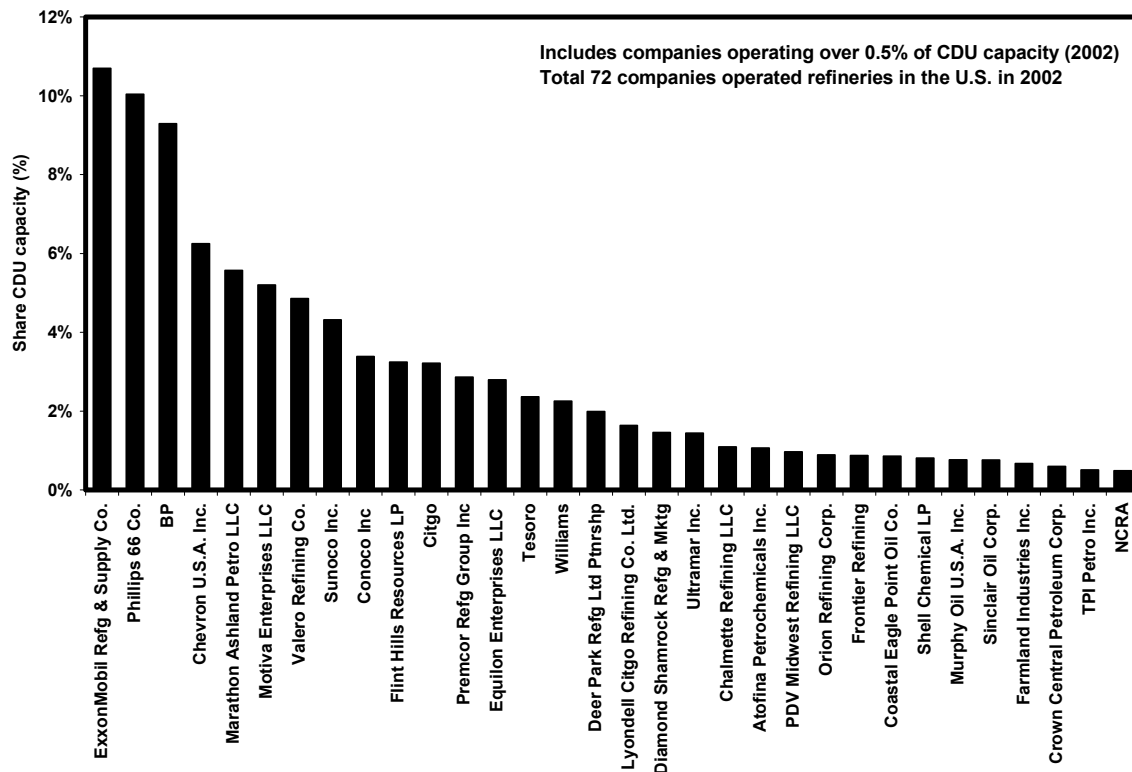

Figure 4. Refining capacity (expressed as percentage of CDU capacity) for companies operating over 0.5% of CDU capacity in 2002. The depicted companies operate 93% of total national capacity. Companies operating less than 0.5% of CDU capacity are not depicted for graphical reasons. Source: Energy Information Administration.

The smaller refineries produce a relative simple mix of products, with an on average lower production value. The share of the economic value of the smaller companies is even smaller than the share of the production capacity.

Total refinery output has increased over time with an average rate of just over 2%/year, with a peak in the 1980's. Since 1995 output has exceeded the peak of the early 1980's. With the increased production, demand for the different types of outputs has changed. Increased demand for lighter products including gasoline and reduced demand for fuel oil have resulted in a considerable change in output mix. Figure 5 depicts the relative share of the different products of U.S. refineries, clearly demonstrating a trend away from heavy fuels and towards lighter products such as gasoline and jet fuel.
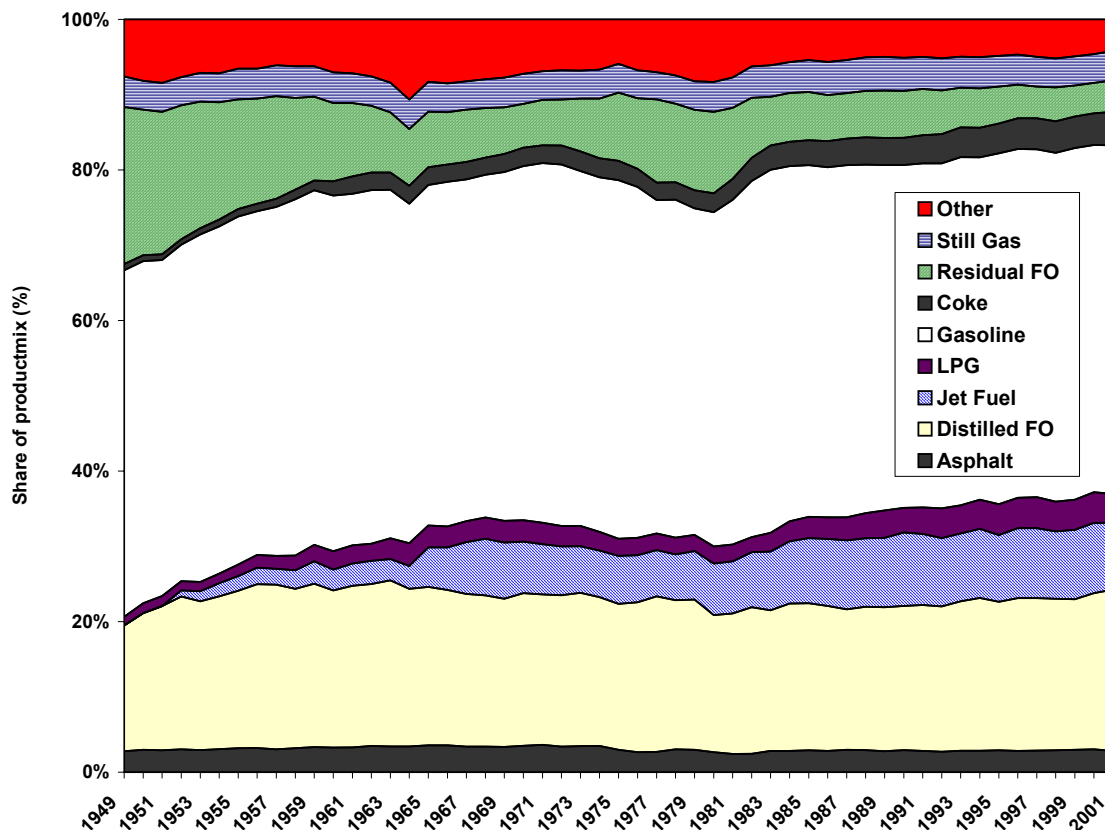
Figure 5. U.S. refinery product mix from 1949 till 2001, expressed as percent of total output. Source: Energy Information Administration.

The increased demand for lighter products has resulted in increased conversion capacity at the refineries over time (see Chapter 3). Increased fuel quality demands have also resulted in a change in the quality of the gasoline produced in some U.S. markets, especially California. Both developments result in increased processing energy needs at the refineries.[1]

This development is likely to increase in the future. However, in the future the U.S. will also need to rely on the use of heavier crude oil types (Swain, 2002), and increased imports of crude oil to meet increasing demand. At the same time, the average sulfur content of processed crude has increased over the past 10 years (Swain, 2002). This will likely result in a further expansion of conversion capacity at US refineries. Increased air quality demands in many parts of the United States will also result in an increased demand for low-sulfur automotive fuels (gasoline, diesel), resulting in an increase of hydrotreating capacity. Smaller refineries will most likely not be able to invest in this type of expansion. With limited markets for the hydroskimming refineries, a further concentration of refineries is likely to take place over the next few years. Expansion of

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[1] Part of the increased energy use is offset by increased efficiency of car engines burning low-sulfur fuel. The low-sulfur gasoline also results in reduced mobile pollutant emissions and improved air quality.

existing refineries will provide the increased demand, and no refineries will likely be built in the next few years.

2.2 The California Petroleum Refining Industry

California has played a central role in the development of the oil industry in the country, starting with the development of the oil fields in Los Angeles and Bakersfield. Today, California still leads the way in refining technology trends due the increased fuel quality demands. After Texas and Louisiana, California has the largest petroleum refining industry in the country. Historically, the industry was located in or near the oil fields. State crude oil production has decreased over the past decades, while processing has increased over the same period. This resulted in increased capacity utilization, as refining capacity decreased in California (see Figure 6).
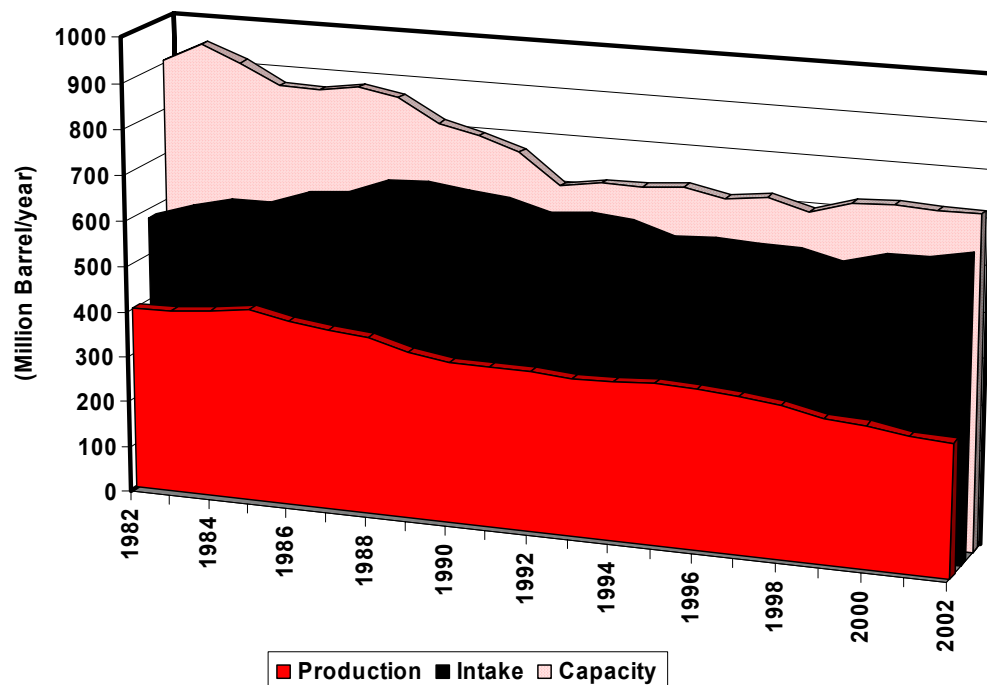
Figure 6. Crude oil production, refinery crude oil intake and capacity in California from 1982 till 2002. Source: California Energy Commission.

Today, the largest refineries are found near easy ocean access to allow for imports of crude oil from various regions in the world. In 2002 California imported 30% of the crude oil consumption from foreign sources. The largest imports were from Iraq, Saudi-Arabia, Ecuador, Mexico, Angola and Argentina. Figure 7 gives an overview of the main sources of crude oil processed in California refineries. It clearly shows an increasing importance of imported oil from foreign countries, and a decrease of Alaska-oil and in-state production. This trend is likely to continue over the next decade (CEC, 1999), especially due to a further decline in the use of Alaska oil. California production is expected to reduce only slightly over the next 15 year. Also, the average gravity and

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sulfur content of oil processed in West-Coast refineries has increased over the past 10 years. These dynamics will influence the future directions of the Californian petroleum refining industry, as well as determine the future technology needs.
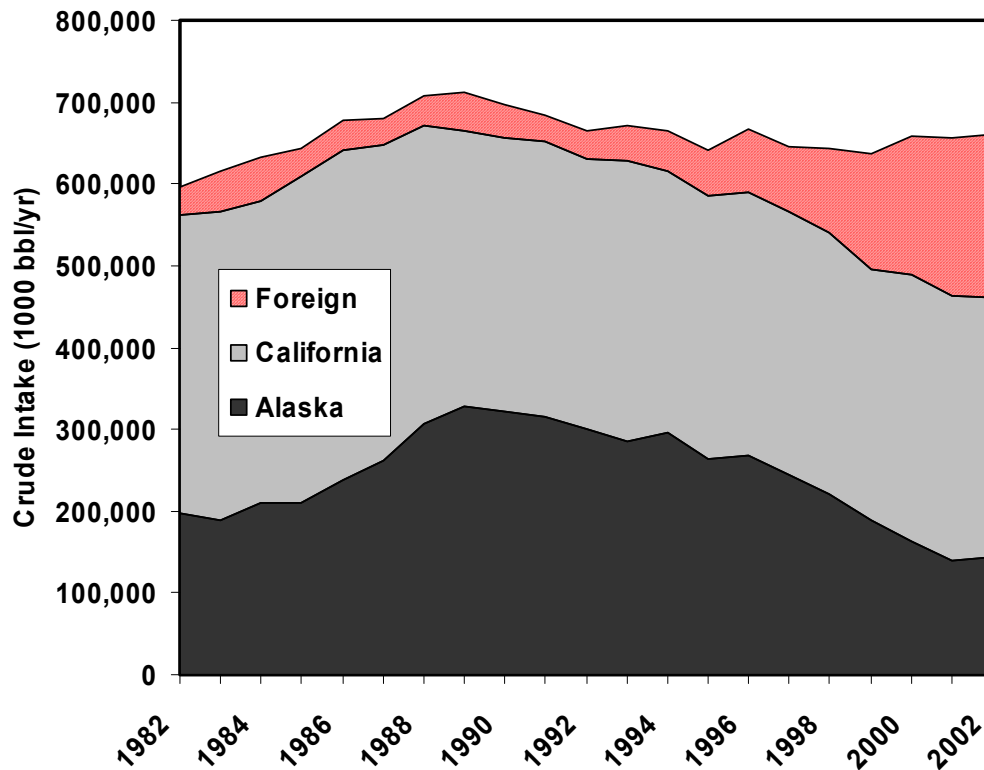
Figure 7. Sources of crude oil processed in California refineries from 1982 till 2002. Source: California Energy Commission.

Large refinery complexes are found in the Los Angeles area, San Francisco Bay Area and the Bakersfield area. Like the trend observed in the United States, the petroleum refinery industry is concentrated more and more in a number of larger integrated refinery complexes. Today, 14 refineries operated by 8 companies produce all the refined oil products in California. Figure 8 depicts the 14 refineries in California by crude-intake capacity.
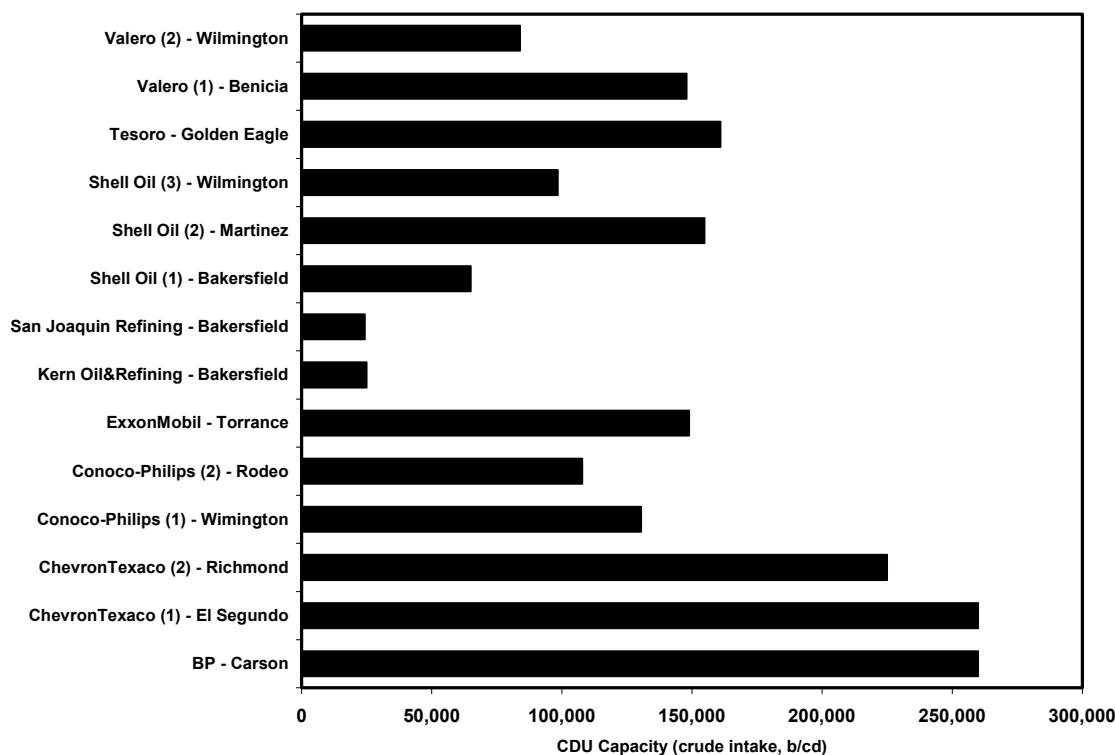
Figure 8. Capacity of operating refineries in 2002 in California, based on Crude Distillation capacity (expressed as barrel/calendar day).

A number of companies operate more than one refinery in California, i.e. ChevronTexaco (26% of capacity in California), Shell (17%), Conoco-Philips (13%), and Valero (12%). Various companies operate a single larger refinery in California, i.e. BP (14%), Tesoro (9%) and ExxonMobil (8%), while two small refineries in the Bakersfield area are still operated by small independent producers. Figure 9 depicts the locations of the refineries in California, demonstrating the current concentration in three areas.

The further concentration of refineries in the U.S. has contributed to a reduction in operating costs but also impacted the refining margins (Killen et al., 2001). The Western U.S. market is more or less isolated from the other primary oil markets in the U.S. Although overall market dynamics in the U.S. and the western market follow the same path, the operating margin from Western refineries is higher than that in other regions. Between 1995 and 2000 the operating margin of West Coast refineries has grown from $3 till a high of $8/bbl crude in 2000 (Killen et al., 2001), compared to 1 to 4$/bbl in other U.S. markets.

The California refineries produce a mix of products that includes a larger fraction of lighter products such as gasoline. Figure 10 compares the 1999 product mix of the petroleum-refining sector in the U.S., the Petroleum Administration for Defense District

V[2], and California. Figure 10 shows that gasoline represents 53% of the California refinery output, whereas it is just below 47% in the U.S. and PADD-V.

Figure 9. Location of petroleum refineries in California. Source: California Energy Commission.

Furthermore, refineries in California produce a larger share of reformulated gasoline and fuels with lower sulfur content. Because of this market in which the California refineries operate, it has a relatively high share of advanced conversion processes; more than most other states. This makes the petroleum refining industry in more energy intensive in its product-mix than the US-average.

Combining the different product-mix with the changing origins of crude oil processed will drive change in the Californian petroleum industry in the foreseeable future. The unique position in the Nation's petroleum refining industry also results in slightly different emphasis on technology development needs.

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[2] The PADD-V district covers the west coast, and consists of Alaska, Arizona, California, Hawaii, Nevada, Oregon and Washington. California produces about 64% of all the output in PADD-V.
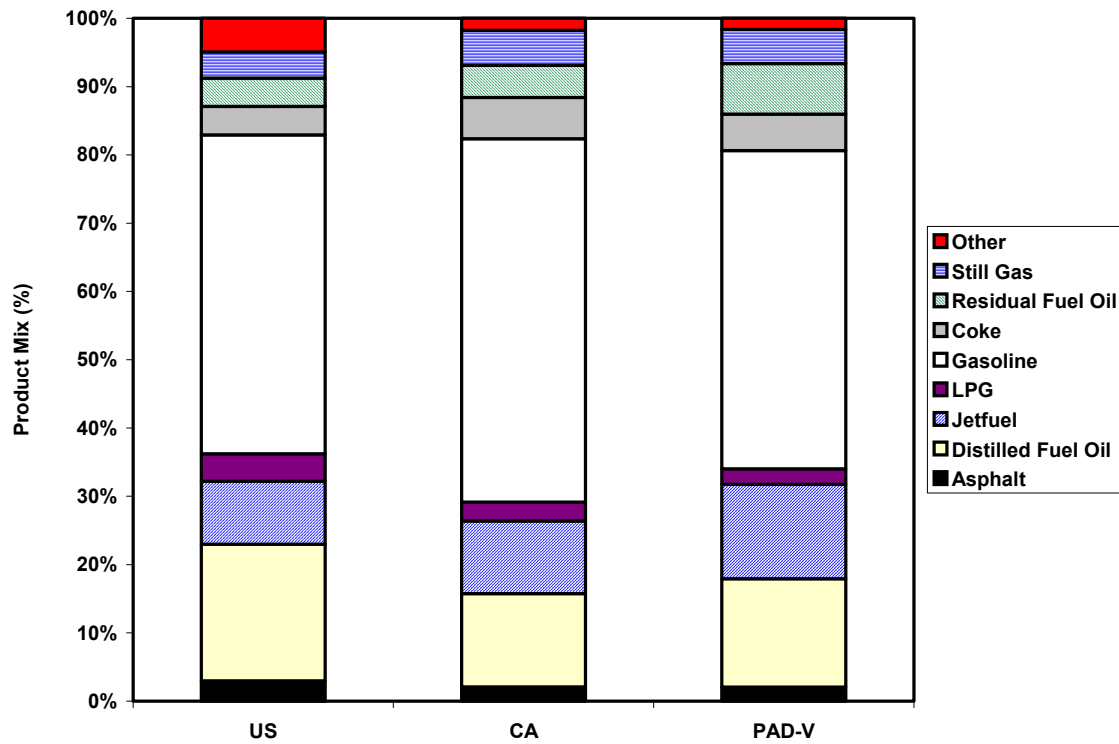
Figure 10. Product-mix composition in the United States, PADD-V district and California in 1999. Sources: Energy Information Administration, California Energy Commission.

3. Process Description

The U.S. has the world's largest refining capacity, processing just less than a quarter of all crude oil in the world. A modern refinery is a highly complex and integrated system separating and transforming crude oil into a wide variety of products, e.g. transportation fuels, residual fuel oils, lubricants, and many other products. The simplest refinery type is a facility in which the crude oil is separated into lighter and heavier fractions through distillations. In the U.S. about 25% of the refinery facilities are small operations producing fewer than 50,000 barrels/day (US DOE-OIT, 1998), representing about 5% of the total industry output. The existence of small, simple and relatively inefficient refineries is in part due to legislation subsidizing smaller operations, following the first oil price shock. These smaller operations consist only of distillation capacity, and no reforming or converting capacities and make a limited number of products.

Modern refineries have developed much more complex and integrated systems in which hydrocarbon compounds are not only distilled but are also converted and blended into a wider array of products. The overall structure of the refinery industry has changed in recent years because of a growing demand for lighter products. This has led to more complex refineries with increased conversion capacities. Increased conversion will lead to an increase in the specific energy consumption but will produce a product-mix with a higher value. These dynamics will continue in the future, as demand for heating (fuel) oil is decreasing.

In all refineries, including smaller simple refineries, the crude oil is first distilled, which is followed by conversion in more complex refineries. The most important distillation processes are the crude or atmospheric distillation, and vacuum distillation. Different conversion processes are available using thermal or catalytic processes. The most important are the catalytic reformer, where the heavy naphtha, produced in the crude distillation unit, is converted to gasoline, and the Fluid Catalytic Cracker where the distillate of the vacuum distillation unit is converted. Newer processes, such as hydrocrackers, are used to produce more light products from the heavy bottom products. Finally, all products may be treated to upgrade the product quality (e.g. sulfur removal using a hydrotreater). Side processes that are used to condition inputs, produce hydrogen or by-products include crude conditioning (e.g. desalting), hydrogen production, power and steam production, and asphalt production. Lubricants and other specialized products may be produced at special locations.

Below we will discuss the main production steps in refineries. We provide a brief process description and the most important operation parameters including energy use. Figure 6 provides a simplified flow scheme of a refinery. We follow the flow scheme, starting with the intake of the crude until the production of the final products. The flow of intermediates between the processes will vary by refinery, and depends on the structure of the refinery, type of crude processes, as well as product mix.
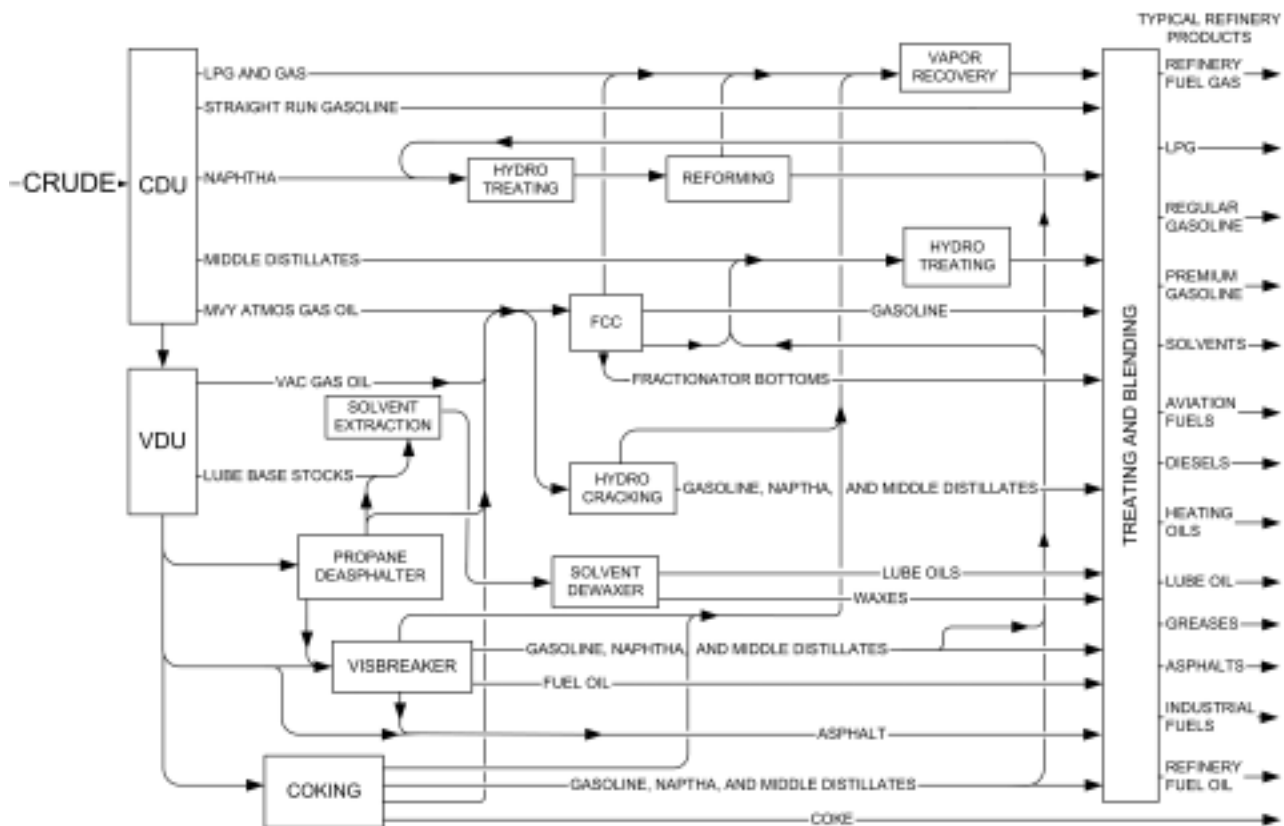
Figure 6. Simplified flowchart of refining processes and product flows. Derived from Gary and Handwerk (1994).

Desalting. If the salt content of the crude oil is higher than 10 lb/1000 barrels of oil, the crude requires desalting (Gary and Handwerk, 1994). Desalting will reduce corrosion and minimize fouling of process units and heat exchangers. Heavier crudes generally contain more salts, making desalting more important in current and future refineries. The salt is washed from the crude with water (3-10% at temperatures of 200-300°F (90-150ºC). The salts are dissolved in the water, and an electric current is used to separate the water and the oil. This process also removes suspended solids. The different desalting processes vary in the amount of water used and the electric field used for separation of the oil and water. The efficiency of desalting is influenced by the pH, gravity, viscosity, salt content of the crude oil, and the volume of water used in the process.

Crude Distillation Unit (CDU). In all refineries, desalted and pretreated crude oil is split into three main fractions according to their boiling ranges by a fractional distillation process. The crude oil is heated in a furnace to approximately 750°F (390ºC), and subsequently fed into the fractionating or distillation tower. Most CDUs have a two-stage heating process; first the hot gas streams of the reflux and product streams are used to heat the desalted crude to about 550°F (290ºC). It is then further heated in a gas-fired furnace to 400ºC (Gary and Handwerk, 1994). The feed is fed is to the distillation tower at a temperature between 650 and 750°F (340-390ºC). Energy efficiency of the heating

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process can be improved by using pump-around reflux to increase heat transfer (at higher temperatures at lower points in the column).

In the tower the different products are separated based on their boiling points. The boiling point is a good measure for the molecule weight (or length of the carbon chain) of the different products. Gasoline, with relative small molecules boils between 70 and 140ºC, while naphtha, which has a larger molecule, has a boiling point between 140 and 180ºC. The distillation towers contains 30-50 fractionation trays. The number of trays depends on the desired number and purity of product streams produced at the particular CDU.

The lightest fraction includes fuel gas, LPG and gasoline. The overhead, the top or lightest fraction of the CDU is a gaseous stream and is used as fuel or for blending.

The middle fraction includes kerosene and diesel oil. The middle fractions are used for the production of gasoline and kerosene. The naphtha is led to the catalytic reformer or used as feedstock for the petrochemical industry.

The heaviest fraction is mainly naphtha and fuel oil, which has the lowest value. Fuel oil can be further processed in the conversion unit to produce more valuable products. About one third of the products of the CDU (on energy basis) cannot be used directly and are fed into the Vacuum Distillation Unit (VDU), where distillation is performed under low pressure.

Because the CDU processes all incoming crude oil, it is a large energy user, although specific energy consumption compared to the conversion process is relatively low. Energy efficiency opportunities consist of improved heat recovery and heat exchange (process integration), improved separation efficiencies and other smaller measures. Integration of heat from the CDU and other parts of the refinery may lead to additional energy savings.

Vacuum Distillation Unit (VDU) or High Vacuum Unit (HVU). The VDU/HVU further distills the heaviest fraction (e.g. heavy fuel oil) from the CDU under vacuum conditions. The reduced pressure decreases the boiling points making further separation of the heavier fractions possible. The heavier fractions from the CDU would need to be cracked at higher temperatures at atmospheric pressures. Therefore, these fractions are processed under vacuum conditions. The low pressure results in much larger process equipment. In the VDU, the incoming feedstream is heated in a furnace to 730-850°F (390-450ºC).

The vacuum conditions are maintained by the use of steam ejectors, vacuum pumps and condensers. It is essential to obtain a very low-pressure drop over the distillation column to reduce operating costs.

Of the VDU products, the lightest fraction becomes diesel oil. The middle fraction, which is light fuel oil, is sent to the Hydrocracker (HCU) or Fluid Catalytic Cracker (FCC), and the heavy fuel oil is sent to the Thermal Cracker.

The distillation products are further processed, depending on the desired product mix. Refinery gas is used as fuel in the refinery operations to generate heat (furnaces), steam (boilers) or power (gas turbines), while some of the refinery gas may be flared. Parts of the refinery gas may also be used to blend with LPG or for hydrogen production. Hydrogen is used in different processes in the refinery to remove sulfur (e.g. hydrotreating) and to convert to lighter products (e.g. hydrocracking).

Hydrotreater. Naphtha and middle-distillates are desulfurized in the hydrotreater and processed in a catalytic reformer. Contaminants such as sulfur and nitrogen are removed from gasoline and lighter fractions by hydrogen over a hot catalyst bed. Sulfur removal is necessary to avoid catalyst poisoning downstream, and to produce a clean product. The treated light gasoline is sent to the Isomerization Unit and the treated heavy gasoline to the catalytic reformer or platformer to have its octane level increased. Hydrotreaters are also used to desulfurize other product streams in the refinery.

Although many different hydrotreater designs are marketed, they all work along the same principle. The feedstream is mixed with hydrogen and heated to a temperature between 500 and 800°F (260-430ºC). In some designs the feedstream is heated and then mixed with the hydrogen. The reaction temperature should not exceed 800°F (430ºC) to minimize cracking. The gas mixture is lead over a catalyst bed of metal oxides (most often cobalt or molybdenum oxides on different metal carriers). The catalysts help the hydrogen to react with sulfur and nitrogen to form hydrogen sulfides (H_2S) and ammonia. The reactor effluent is then cooled, and the oil feed and gas mixture is then separated in a stripper column. Part of the stripped gas may be recycled to the reactor.

In the hydrotreater, energy is used to heat the feedstream, and power to transport the flows. The hydrotreater also has a significant indirect energy use because of the consumption of hydrogen. In the refinery most hydrogen is produced through reforming (see below) and some as a by-product of distillation.

Catalytic Reformer. The reformer is used to increase the octane level in gasoline. The desulfurized naphtha and gasoline streams are sent to the catalytic reformer. The product, called reformate, is used in blending of different refinery products. The catalytic reformer produces around 30-40% of all the gasoline produced in the U.S. Because the catalytic reformer uses platinum as catalyst, it needs to be desulfurized to reduce the danger of catalyst poisoning.

Reforming is undertaken by passing the hot feed stream through a catalytic reactor. In the reactor, various reactions such as dehydrogenation, isomerization and hydrocracking occur to reformulate the chemical formulas of the stream. Some of the reactions are endothermic and others exothermic. The types of reactions depend on the temperature, pressure and velocity in the reactor. Undesirable side-reactions may occur and need to be limited. The reformer is a net producer of hydrogen that is used elsewhere in the refinery.

Various suppliers and developers market a number of reforming processes. In principle all designs are continuous, cyclic or semi-regenerative, depending on the frequency of catalyst regeneration (Gary and Handwerk, 1994). In the continuous process, the catalysts can be replaced during normal operation, and regenerated in a separate reactor. In the semi-regenerative reactor, the reactor needs to be stopped for regeneration of the catalysts. Depending on the severity and operating conditions, the period between regenerations is between 3 and 24 months (Gary and Handwerk, 1994). The cyclic process is an alternative in between these two processes. The advantage of the semi-regenerative process is the low capital cost. The marketed processes vary in the reactor design.

Fluid Catalytic Cracker (FCC). The fuel oil from the CDU is converted into lighter products over a hot catalyst bed in the Fluid Catalytic Cracker (FCC). The FCC is the most important and widely used conversion process in refineries. The FCC produces high-octane gasoline, diesel and fuel oil. The FCC is mostly used to convert heavy fuel oils into gasoline and lighter products. The FCC has virtually replaced all thermal crackers.

In a fluidized bed reactor filled with particles carrying the hot catalyst and a preheated feed (500-800°F, 260-425ºC), at a temperature of 900-1000°F (480-540ºC) the feed is 'cracked' to molecules with smaller chains. Different cracking products are generated, depending on the feed and conditions. During the process, coke is deposited on the catalysts. The used catalyst is continuously regenerated for reuse, by burning off the coke to either a mixture of carbon monoxide (CO) and carbon dioxide (CO_2) or completely to CO_2. If burned off to a CO/CO_2-mixture, the CO is combusted to CO_2 in a separate CO-burning waste heat recovery boiler to produce steam. The regeneration process is easier to control if the coke is burned directly to CO_2, but a waste heat recovery boiler should be installed to recover the excess heat in the regenerator. The cracking reactions are endothermic, while the regeneration is exothermic, providing an opportunity for thermal integration of the two process steps.

Older FCCs used metal catalysts, while new FCC designs use zeolite catalysts, which are more active. This has led to a re-design of modern FCC units with a smaller reactor, and most of the reactions taking place in the so-called riser, which leads the hot feed and regenerated catalysts to the reaction vessel. The different FCC designs on the market vary in the way that the reactor and regeneration vessels are integrated. Varying the catalyst circulation rate controls the process.

FCCs are net energy users, due to the energy needed to preheat the feed stream. However, modern FCC designs also produce steam and power (if power recovery turbines are installed) as by-products. The power recovery turbines can also be used to compress the air for the cracker. The recovery turbine is installed prior to the CO or waste heat boiler, if the FCC works at pressures higher than 15 psig (Gary and Handwerk, 1994).

Hydrocracker (HCU). The Hydrocracker has become one of the most important processes in the modern refinery to allow for flexibility in product-mix. The hydrocracker

provides a better balance of gasoline and distillates, improves gasoline yield, octane quality, and can supplement the FCC to upgrade heavy feedstocks (Gary and Handwerk, 1994). In the hydrocracker, light fuel oil is converted into lighter products under a high hydrogen pressure and over a hot catalyst bed. The main products are naphtha, jet fuel and diesel oil. It may also be used to convert other heavy fuel stocks to lighter products. The hydrocracker concept was developed before World War II to produce gasoline from lignite in Germany, but it has been further developed in the early 1960's by Chevron. Now it can be found in many modern large refineries around the world.

In the hydrocracker many reactions take place. The principal reactions are similar to that of a FCC, although *with* hydrogenation. The reactions are carried out at a temperature of 500-750°F (290-400ºC) and increased pressures of 8.3 to 13.8 Bar. The temperature and pressures used may differ with the licensed technology. The reactions are catalyzed by a combination of rare earth metals. Because the catalyst is susceptible to poisoning, the hydrocracker feed needs to be prepared by removing metallic salts, oxygen, nitrogenous compounds and sulfur. This is done by first hydrogenating the feed, which also saturates the olefins. This is an exothermic reaction, but insufficient to provide all the heat for the hydrotreating units of the cracker. The nitrogen and sulfur-compounds are removed in a stripper column, while water is removed by a molecular sieve dryer or silica gel.

The prepared feed is mixed with recycled feed and hydrogen, and preheated before going to the reactor. The reactions are controlled by the temperature, reactor pressure, and velocity. Typically the reactor is operated to have a conversion efficiency of 40-50%, meaning that 40-50% of the reactor product has a boiling point below 400F (205ºC). The product flow (effluent) is passed through heat exchangers and a separator, where hydrogen is recovered for recycling. The liquid products of the separator are distilled to separate the C_4 and lighter gases from the naphtha, jet fuel and diesel. The bottom stream of the fractionator is mixed with hydrogen and sent to a second-stage reactor to increase the conversion efficiency to 50-70% (Gary and Handwerk, 1994).

Various designs have been developed and are marketed by a number of licensors in the U.S. and Western Europe. The hydrocracker consumes energy in the form of fuel, steam and electricity (for compressors and pumps). The hydrocracker also consumes energy indirectly in the form of hydrogen. The hydrogen consumption is between 150-300 scf/barrel of feed (27-54 Nm^3/bbl) for hydrotreating and 1000 and 3000 scf /barrel of feed (180-540 Nm^3/bbl) for the total plant (Gary and Handwerk, 1994). The hydrogen is produced as side-product of the catalytic reformer and in dedicated steam reforming plants (see below).

Coking. A new generation of coking processes has added additional flexibility to the refinery by converting the heavy bottom feed to lighter feedstocks and coke. Coking can be considered as a severe thermal cracking process. The modern coking processes are mainly used to prepare a feed for the hydrocracker (see above). The most important processes are Fluid Coking and Fexicoking (both developed by Exxon) and used at various refineries around the world.

We focus on the Flexicoking process. In the Flexicoking process a heavy feed is preheated to 600-700°F (315-370ºC) and sprayed on a bed of hot fluidized coke (recycled internally). The coke bed has a reaction temperature between 950 and 1000°F (510-540ºC). At this temperature cracking reactions take place. Cracked vapor products are separated in cyclones and are quenched. Some of the products are condensed, while the vapors are led to a fractionator column, which separate various product streams.

The coke is stripped from other products, and then processed in a second fluidized bed reactor where it is heated to 1100°F (590ºC). The hot coke is then gasified in a third reactor in the presence of steam and air to produce synthesis gas. Sulfur (in the form of H_2S) is removed, and the synthesis gas (mainly consisting of CO, H_2, CO_2 and N_2) can be used as fuel in (adapted) boilers or furnaces.

The coking unit is a consumer of fuel (in preheating), steam and power.

Visbreaker. Visbreaking is a relatively mild thermal cracking operation, used to reduce the viscosity of the bottom products to produce fuel oil. This reduces the production of heavy fuel oils, while the products can be used to increase FCC feedstock and increase gasoline yields. This is accomplished by cracking the side chains of paraffin and aromatics in the feed, and cracking of resins to light hydrocarbons. Depending on the severity (i.e. time and temperature in the cracker) of the reactions different products may be produced.

There are two main processes: coil (or furnace) and soak cracking. Coil cracking uses higher reactor temperatures and shorter residence times, while soak cracking has slightly lower temperatures and longer residence times (Gary and Handwerk, 1994). The reaction products are pretty similar, but the soaker cracker uses less energy due to the lower temperature, and has longer run times (due to reduced coke deposition on the furnace tubes). A soaker furnace consumes about 15% less energy than a coil furnace. The visbreaker consumes fuel (to heat the feed), steam and electricity.

Alkylation and Polymerization. Alkylation (the reverse of cracking) is used to produce alkylates (used in jet fuel), as well as butane liquids, LPG and a tar-like by-product. The reactions are catalyzed by either hydrofluoric acid or sulfuric acid. Several designs are used, using either of the catalysts. The most suitable alkylation process for a given refinery is determined by economics, especially with regard to the costs of acid purchase and disposal (Gary and Handwerk, 1994).

Alkylation processes use steam and power. There are no large differences in energy intensity between both processes (Gary and Handwerk, 1994).

Hydrogen Manufacturing Unit or Steam reforming (HMU). There are a number of supporting processes, that do not produce the main refinery products directly, but produce intermediates used in the various refining processes. Hydrogen is generated from natural gas and steam over a hot catalyst bed, similar to the processes used to make hydrogen for ammonia.

Hydrogen is produced by steam reforming the natural gas feedstock with steam over a catalyst, producing synthesis gas. Synthesis gas contains a mixture of carbon monoxide and hydrogen. The carbon monoxide is then reacted with steam in the water-gas-shift reaction to produce carbon dioxide and hydrogen. The carbon dioxide is removed from the main gas stream using absorption, producing hydrogen.

Energy is used in the form of fuel (to heat the reformer), steam (in the steam reforming) and power (for compression). Many different licensors supply the technology. Modern variants use a physical adsorption process to remove CO_2, which uses less energy than chemical absorption processes.

Gas Processing Unit. Refinery gas processing units are used to recover C_3, C_4, C_5 and C_6 components from the different processes, and produce a desulfurized gas which can be used as fuel or for hydrogen production in steam reforming (see above). The lighter products are used as fuel or for H2 production, while the heavier fraction is recycled in the refinery.

The process consists of a number of distillation, absorption and stripper columns to recover the ethane, propane and butane. The process uses fuel (to heat the incoming gas) and power (for compressors and other uses).

Acid Gas Removal. Acid gases such as H_2S and CO_2 need to be removed to reduce air pollution (before 1970, they were just burned off) and are produced as a by-product of producing higher quality refinery products. These gases are removed by an (chemical) absorption process, and then further processed. H_2S can be processed into elemental sulfur through the Claus process. The process consumes fuel and electricity, but the Claus process produces low-pressure steam (1.7 bar).

Bitumen Blower (BBU). Heavy fuel oil of some heavy crude oil is blown with hot air to produce bitumen or asphalt.

Other processes may be used in refineries to produce lubricants (lube oil), petrochemical feedstocks and other specialty products. These processes consist mainly of blending, stripping and separation processes. We do not discuss them in detail here, as these are not found in a large number of refineries.

Table 1 and Figure 12 provide an overview of the processing capacities of the different processes used in U.S. refineries, based on the capacity per January 1st, 2003. The distribution of the processes will vary by state depending on the type of crudes used and products produced. For example, California has a much higher capacity (relative to CDU-capacity) of hydrocracking and hydrotreating, when compared to the U.S. average. This is due to the relative higher desired output of lighter products (e.g. gasoline) and the regulatory demand for lower sulfur-content from gasoline to reduce air pollution from transport. On the other hand, Californian refineries do not produce any aromatics as a chemical feedstock, as no large petrochemical industry is present in the state.
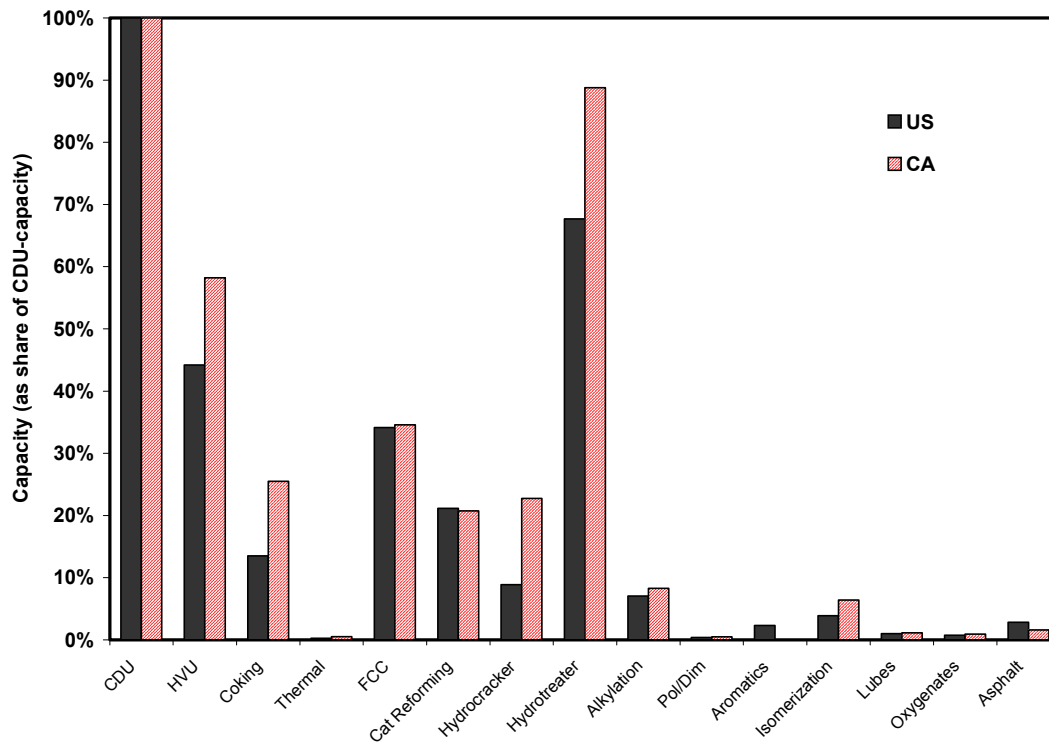
Figure 12. Capacity distribution of the major refining processes in U.S. and Californian petroleum refineries, expressed as share of installed CDU capacity, as of January 1st, 2003. Source: Oil & Gas Journal (2002).

Table 1. Capacity distribution of the major refining processes in U.S. and Californian petroleum refineries, as of January 1st, 2003. The distribution is also given as share of CDU capacity. Source: Oil & Gas Journal (2002).

Process	Capacity (Barrel per calendar day)		Distribution (share of CDU capacity)	
	U.S.	California	U.S.	California
Crude Distillation	16,623,301	1,893,020	100.0%	100.0%
Vacuum Distillation	7,347,704	1,102,209	44.2%	58.2%
Coking	2,243,947	482,602	13.5%	25.5%
Thermal Operations	43,500	10,000	0.3%	0.5%
Catalytic Cracking	5,677,355	654,700	34.2%	34.6%
Catalytic Reforming	3,512,237	402,700	21.1%	21.3%
Hydrocracking	1,474,710	430,450	8.9%	22.7%
Hydrotreating	11,247,745	1,680,813	67.7%	88.8%
Alkylation	1,170,019	118,900	7.0%	6.3%
Polymerization/Dim.	64,000	9,400	0.4%	0.5%
Aromatics	383,255	0	2.3%	0.0%
Isomerization	644,270	121,300	3.9%	6.4%
Lubes	167,500	21,500	1.0%	1.1%
Oxygenates	122,899	17,400	0.7%	0.9%
Asphalt	471,850	30,100	2.8%	1.6%
Hydrogen *(MMcfd)*	*3,631*	1,303	-	-
Coke *(tpd)*	*114,387*	21,746	-	-
Sulfur *(tpd)*	*27,051*	3,775	-	-

Figure 13 provides the breakdown of the process capacity for the 14 operating refineries in California. The small refineries have only limited processing capabilities, while the larger refineries have invested in processes to upgrade the heavier fraction into lighter products and produce cleaner fuels (e.g. a relative large capacity of hydrotreaters relative to crude distillation capacity).
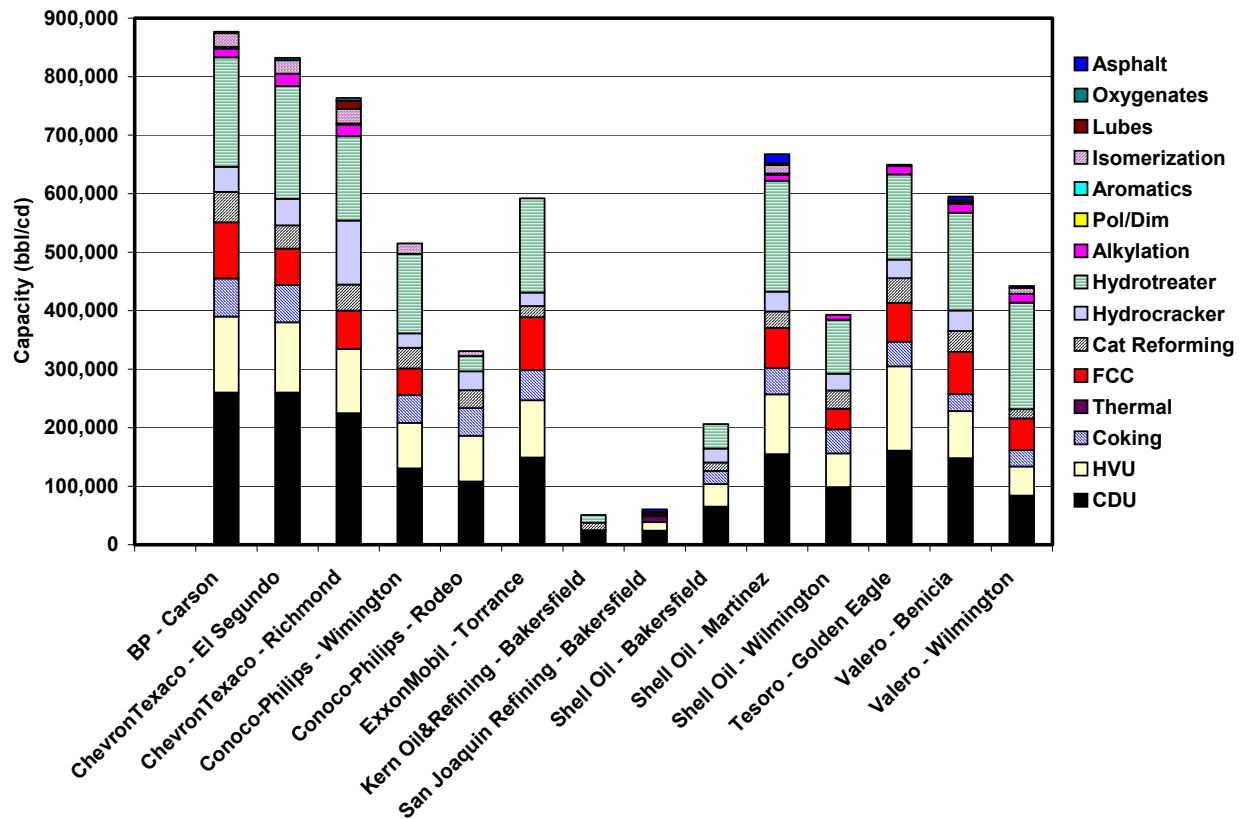

Figure 13. Process breakdown for the 14 operating refineries in California (as of January 1st, 2003), expressed as capacity (bbl/calenderday). Source: Oil & Gas Journal.

4. Energy Consumption

4.1 Energy Use of Refineries in the United States

The petroleum refining industry is one of the largest energy consuming industries in the United States, and in many states. Energy use in a refinery varies over time due to changes in the type of crude processed, the product mix (and complexity of refinery), as well as the sulfur content of the final products. Furthermore, operational factors like capacity utilization, maintenance practices, as well as age of the equipment affect energy use in a refinery from year to year.

The petroleum refining industry is a very energy intensive industry spending over $7 Billion on energy purchases in 2001. Figure 14 depicts the trend in energy expenditures of the petroleum refining industry. The graph shows a steady increase in total expenditures for purchased electricity and fuels, which is especially evident in the most recent years fro which data is available. More importantly is the increasing share of energy costs compared to the value added produced by petroleum refining, underlining a decreasing energy productivity of refining operations. Value added as share of value of shipments dipped in the early 1990's and has increased since to about 20%. Figure 14 also shows a steady increase in fuel costs. Electricity costs are more or less stable, which seems to be only partially caused by increased cogeneration as well.
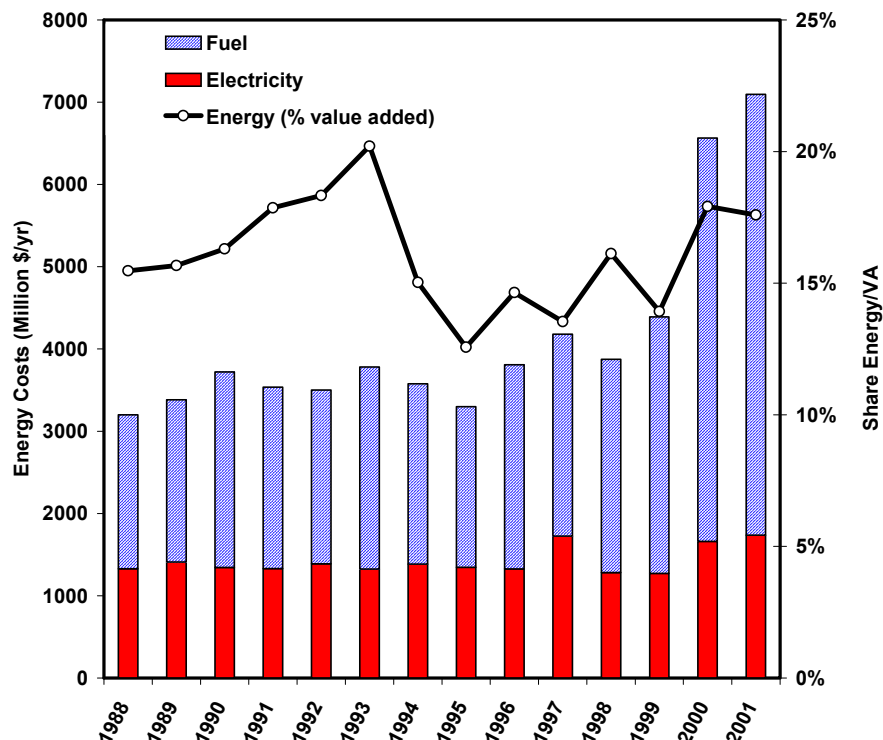

Figure 14. Annual energy costs of petroleum refineries in the United States 1988-2001. Costs are given for purchased fuels and purchased electricity. The total energy purchase costs are given as share of the value added produced by petroleum refineries. Source: U.S. Census, Annual Survey of Manufacturers.

In recent years, energy consumption in refineries peaked in 1998, and has since then slightly declined. Based on data published by the Energy Information Administration we estimate energy consumption trends (by fuel) since 1995.[3] In 2001, the latest year for which data was available, total final energy consumption is estimated at 3025 TBtu (or 3191 PJ). Primary energy consumption[4] is estimated at 3098 TBtu (or 3268 PJ). The difference between primary and final electricity consumption is relatively low due to the small share of electricity consumption in the refinery and relatively large amount of self-produced electricity. Figure 15 depicts the annual energy consumption of petroleum refineries between 1995 and 2001.
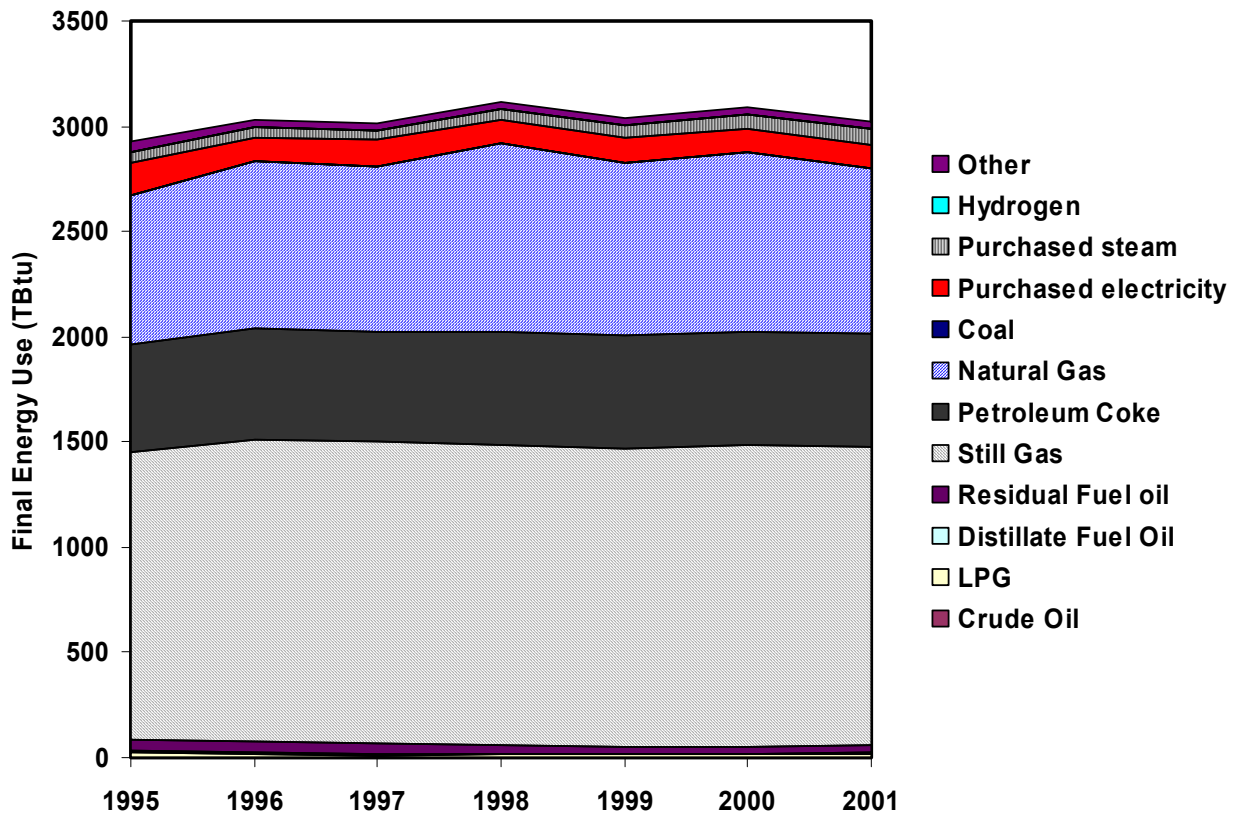
Figure 15. Annual final energy consumption of U.S. petroleum refineries for the period 1995 – 2001. Data for 1995 and 1997 contains estimated values for natural gas, coal, electricity and steam purchases. Source: Petroleum Supply Annual, Energy Information Administration.

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[3] Data before 1995 are also available. However, for some years (including 1995 and 1997) the data reported by EIA is not complete, and interpolations were made by the authors to estimate total energy consumption. For example, for 1995 EIA did not report on consumption of natural gas, coal, purchased electricity and purchased steam, while for 1997 it did not report on coal, purchased steam and other fuels. Furthermore, we use electricity purchase data as reported by the EIA, although the U.S. Census reports slightly different electricity purchases for most years. The differences are generally small and do not affect overall energy use data.

[4] Primary energy consumption includes the losses of offsite electricity and steam production. We assume an average efficiency of power generation on the public grid of 32%. Steam generation efficiency is supposed to be similar to that of refinery boilers (assumed at 77%).

Figure 15 shows that the main fuels used in the refinery are refinery gas, natural gas and coke. The refinery gas and coke are by-products of the different processes. The coke is mainly produced in the crackers, while the refinery gas is the lightest fraction from the distillation and cracking processes. Natural gas and electricity represents the largest purchased fuels in the refineries. Natural gas is used for the production of hydrogen, fuel for co-generation of heat and power (CHP) and as supplementary fuel in furnaces.

Petroleum refineries are one of the largest co-generators in the country, after the pulp and paper and chemical industries. In 1998 co-generation within the refining industry represented almost 13% of all industrial co-generated electricity. (EIA, 2001). Cogeneration peaked in 2001 at almost 35%. In 2001 the petroleum refining industry generated about 13.2 TWh, which represented about 26% of all power consumed on site (EIA, 2002). Figure 16 shows the historic development of electricity generation and purchases in oil refineries (generation data for 2000 was not reported by the U.S. Census).
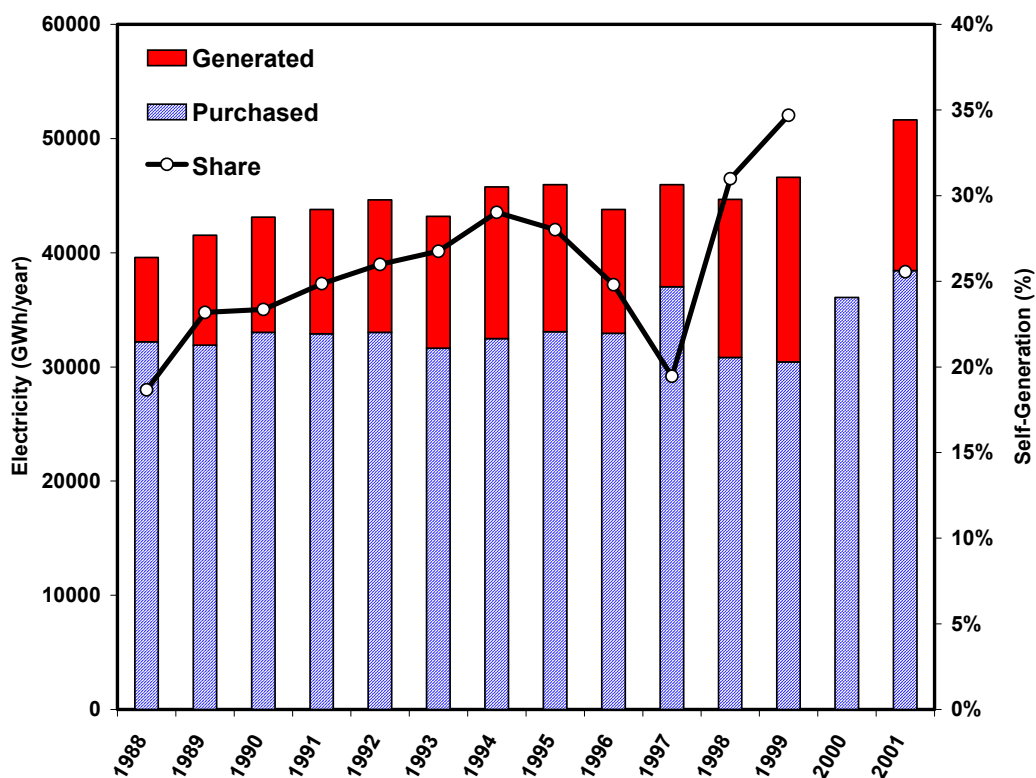
Figure 16. Electricity purchases and generation by petroleum refineries from 1988 till 2001. On the right-hand axis the share of self-generation is expressed as function of total power consumption. Source: U.S. Census, Annual Survey of Manufacturers.

A number of key processes are the major energy consumers in a typical refinery, i.e. crude distillation, hydrotreating, reforming, vacuum distillation and catalytic cracking. Hydrocracking and hydrogen production are growing energy consumers in the refining industry. We have tried to develop an energy balance for refineries for 2001, based on

publicly available data on process throughput (EIA, 2002), specific energy consumption (Gary and Handwerk, 1994; US DOE-OIT, 1998a, US DOE-OIT, 2002) and energy consumption data (EIA, 2001; EIA, 2002; US Census, 2003). Table 2 provides the estimated energy balance for 2001. The energy balance is an estimate based on publicly available data, and is based on many assumptions on process efficiencies and throughputs. The estimated energy balance matches with available energy consumption data for almost 100% on a final energy basis, and almost 98% on a primary energy basis. The process energy uses should be seen as approximate values to provide a view on the most important energy using processes in the refinery.

Table 2. Estimated 2001 energy balance for the U.S. petroleum refining industry. Estimates are based on a combination of publicly available data sources. The energy balance for an individual refinery will be different due to different process configurations. Data sources are given in the text.

Process	Throughput	Fuel	Steam	Electricity	Final	Primary
	Million bbl/day [1]	TBtu	TBtu	GWh	TBtu [2]	TBtu [3]
Desalter	5313.3	0.2	0.0	265.7	1.1	3.0
CDU	5313.3	382.6	245.0	3613.0	713.1	739.3
VDU	2416.7	116.0	126.7	845.8	283.5	289.6
Thermal Cracking	723.4	123.6	-10.5	4630.0	125.7	159.3
FCC	1885.4	108.2	0.5	7013.8	132.8	183.7
Hydrocracker	507.2	68.5	36.9	5873.4	136.5	179.1
Reforming	1166.0	209.8	101.3	3416.3	353.0	377.8
Hydrotreater	3679.8	257.2	270.1	15823.4	661.9	776.7
Deasphalting	112.5	16.1	0.3	213.8	17.2	18.8
Alkylates	366.8	13.2	121.1	2772.7	179.9	200.0
Aromatics	97.2	11.7	4.1	291.5	18.0	20.1
Asphalt	284.9	59.6	0.0	740.7	62.1	67.5
Isomers	204.3	90.3	39.9	398.3	143.5	146.4
Lubes	67.8	87.5	2.5	1247.0	95.0	104.1
Hydrogen	595.9	26.8	0.0	89.4	27.1	27.8
Sulfur	9.0	0.0	-81.2	108.5	-105.1	-104.3
Other		*105.0*	*60.0*	*39.0*	*183.1*	183.3
Total Process Site Use		**1676**	**917**	**47382**	**3029**	**3372**
Purchases			78.4	34187		
Site Generation			838.5	13195		
Cogeneration [4]		140.7	61.9			
Boiler generation [5]			776.5			
Boiler fuels		1008.5	1008.5			
Total Energy Consumption		**2825**	**78**	**34187**	**3020**	**3293**

Notes:
1. Unit is million barrels/year, except for hydrogen (Million lbs/year) and sulfur (million short tons/year).
2. Final fuel use is calculated by estimating the boiler fuel to generate steam used. Electricity is accounted as site electricity at 3412 Btu/kWh.
3. Primary fuel use includes the boiler fuel use and primary fuels used to generate electricity. Including transmission and distribution losses the electric efficiency is 32%.
4. Cogeneration is assumed to be in large singe-cycle gas turbines with an electric efficiency of 32%.
5. Boiler efficiency is estimated at 77%.

Figure 17 summarizes the results of Table 2, depicting the final energy consumption for the different processes.
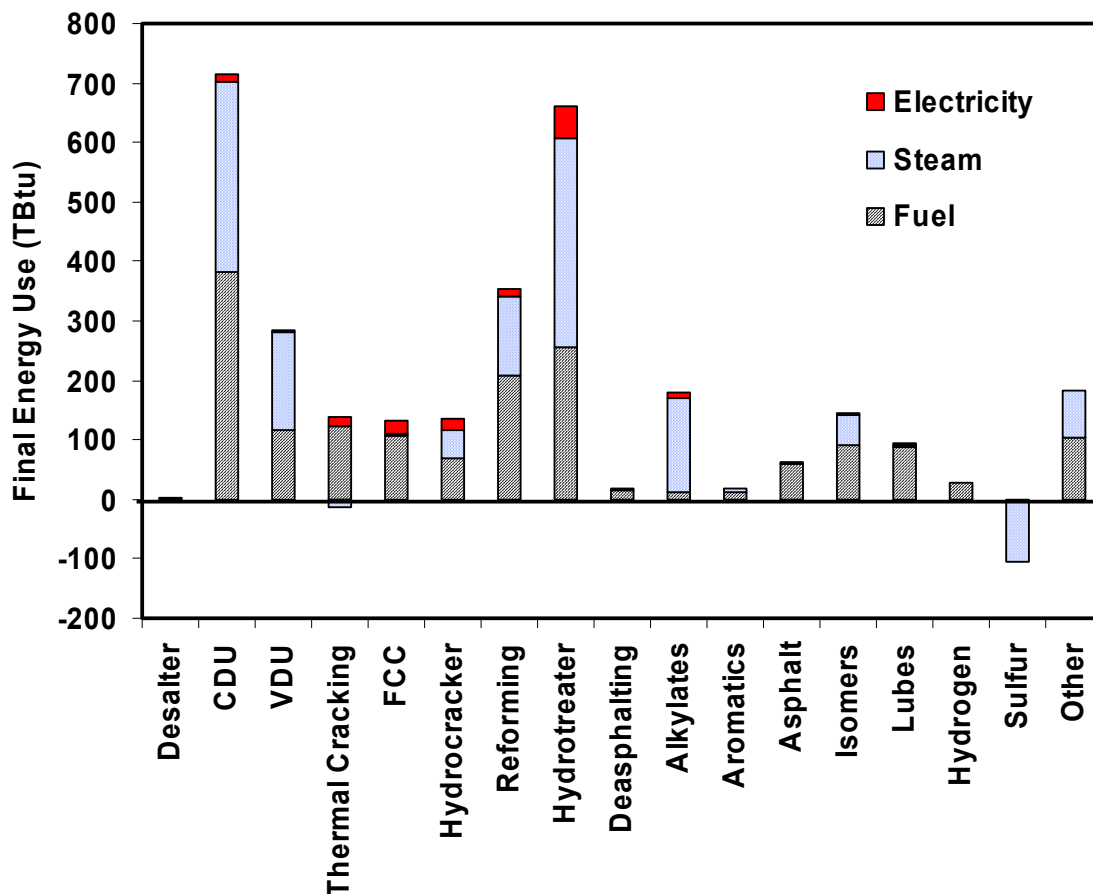
Figure 17. Estimated energy use by petroleum refining process. Energy use is expressed as final energy consumption. Electricity is converted to fuel using 3412 MBtu/kWh. All steam is assumed to be generated at refineries (in reality about 8% is purchased).

The major energy consuming processes are the crude distillation, followed by the hydrotreater, reforming, and vacuum distillation. This is followed by a number of processes consuming a somewhat similar amount of energy, i.e. thermal cracking, catalytic cracking, hydrocracking, alkylate and isomer production.

Note that the figures in Table 2 and Figure 17 are based on publicly available data. We assumed a similar load for all installed processes, based on the average national capacity utilization. In reality the load of the different processes may vary which may lead to a somewhat different distribution. In cracking the severity and in hydrotreating the treated feed may affect energy use. We assumed an average for both factors. Furthermore, energy intensity assumptions are based on a variety of sources, and balanced on the basis of available data. The different literature sources provide varying assumptions for some processes, especially for electricity consumption.

4.2 Energy Use of Refineries in California

The Californian petroleum-refining sector is approximately 11% of the United States refining industry, expressed on the basis of CDU capacity. However, as discussed in Chapter 3 the petroleum refineries in California feature a different, more energy intensive, production structure than the U.S. average due to differences in product mix and degree of hydrotreating. Hence, energy use in Californian refineries is expected to be higher than the share of the national production. Although some of this additional needed energy use may be offset by relative higher efficiency, this is not expected to be a major contribution, as most refineries are not relatively younger than the U.S., reflecting the history of oil exploration and processing in the state.

There is no publicly available data on energy consumption in refineries in California. The Energy Information Administration of the US Department of Energy reports energy consumption data on the aggregation levels of so-called PADDs (Petroleum Administration Defense Districts). The U.S. contains five PADDs, and California is part of PADD V. PADD V contains refineries in Alaska, Arizona, California, Hawaii, Nevada, Oregon and Washington. California refineries represent almost 64% of the crude intake capacity in PADD V. Similar to the differences in processing between the U.S. and California, there are similar large differences between the refinery industry process structure of PADD V and California. For example, while California represents 64% of the crude intake capacity in PADD V, it has 83% of the hydrotreating and 85% of hydrocracking capacity (both energy intensive processes). Final energy consumption in PADD V is approximately 570 TBtu, as given in Table 3.

Table 3. Energy consumption by petroleum refineries in PADD V (Alaska, Arizona, California, Hawaii, Nevada, Oregon and Washington). Source: Energy Information Administration.

Fuel	Energy Use (TBtu)
Crude Oil	0
LPG	10.5
Distillate Fuel Oil	1.6
Residual Fuel Oil	5.4
Still Gas	290.7
Petroleum Coke	86.5
Natural Gas	126.7
Coal	0
Electricity (purchased)	(4695 MWh) 16.0
Steam (purchased)	24.4
Hydrogen	0
Other	8.2
Total	**570.1**

Hence, neither national nor PADD V data can be used directly to make an estimate of energy use in Californian petroleum refineries. Publicly available data on refineries in California includes data on installed process capacity (Oil & Gas Journal, EIA), product

mix[5] (California Energy Commission), as well as data on purchased natural gas and electricity (utilities, California Energy Commission).

Using a "bottom-up method" to estimate energy use on the basis of process distribution and U.S. average energy intensities (as derived in Section 4.1) does not provide a reliable estimate of total energy consumption, when compared to total energy consumption in PADD V. For our estimate of energy use in Californian refineries we will use a "bottom-up method" tailored to all available data for PADD V and California. This will provide the most reliable estimate except for direct reporting by the refineries.

Table 4 provides our estimate of energy use in Californian refineries for 2001. The estimate is based on combination of data from different sources and assumptions on process throughput and process energy intensities. The estimate can be further improved in consultation with the industry.

Table 4. Estimated energy consumption of petroleum refineries in California (2001).

Process	Capacity b/cd	Fuel TBtu	Steam TBtu	Electr. GWh	Final TBtu	Primary TBtu
Desalter	1978132	0	0	32	0	0
CDU	1978132	46	27	322	83	84
VDU	1156155	18	20	132	44	45
Thermal Cracking	381468	11	-2	546	10	13
FCC	650588	12	0	787	15	18
Hydrocracker	476334	21	11	1794	42	49
Reforming	409173	33	6	390	42	43
Hydrotreater	1576697	35	22	1282	67	72
Deasphalting	47767	2	0	30	2	2
Alkylates	150944	2	14	226	20	21
Aromatics	1433	0	0	1	0	0
Asphalt	73354	5	0	62	5	5
Isomers	81682	12	5	52	19	19
Lubes	30953	11	0	161	12	13
Hydrogen	6417226	94	0	313	95	96
Sulfur	4037	0	-12	16	-15	-15
Other	0	13	7	950	25	29
Total	0	315	98	7094	467	496

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[5] This monthly report includes data on the production of coke and still gas, which are important fuels for refineries. However, it does not provide data of consumption of these fuels at the refineries. Based on a comparison of coke and still gas consumption in PADD V and production in California we concluded that a large part of the coke in California is sold and that part of the still gas may also be sold or flared.

5. Energy Efficiency Opportunities and Technology Development

5.1 Introduction

The previous sections have shown that the Californian petroleum industry is leading the country in the production of high-quality fuels. This has resulted in a higher demand for hydrogen-technologies and conversion technologies. Forecasts of future developments in the petroleum refining industry highlight this trend to continue for the U.S. and California, starting with new low-sulfur requirements for diesel (Penning, 2001). The continued trend towards low-sulfur fuels and changes in the productmix of refineries will affect technology choice and needs. For example, the current desulfurization and conversion technologies use relative large amounts of hydrogen. Hydrogen is an energy intensive product. The increased hydrogen consumption will lead to increased energy use and operation expenses, unless more efficient technologies for hydrogen production and recovery are developed and applied. On the long-term new desulfurization technologies may reduce the need for hydrogen. At the same time refineries in California, and increasingly around the nation are faced by challenges to reduce air pollution and other energy related issues (e.g. regulatory changes of power supply, climate change). The petroleum refining industry will face many other challenges. Climate change, new developments in automotive technology, and biotechnology are posed to affect the future structure of refineries. Table 5 summarizes the challenges to the petroleum refining industry.

Table 5. Key Drivers and Challenges for the Californian Petroleum Refining Industry.

Challenge	Key Issues
Fuel Quality	Sulfur, MTBE-replacement
Feedstock	Increasing demand for lighter products from decreasing quality crude
Energy	Costs of power and natural gas
Environment	Emissions of criteria air pollutants (NOx, VOC) and greenhouse gases
Profitability	Commodity market, further concentration of the industry
Safety	Safety incidents, refineries now mainly located in urbanized areas

Katzer et al. (2000) explored the forces of change and the impacts on the future of petroleum refining. They see important new development needs in catalysis, optimization and control, reaction engineering and reactor design, biotechnology for desulfurization, increased use of natural gas as feedstock, and power generation. In the view of Katzer et al. the refinery of the future will look more like an automated chemical plant that will maximize high-value products (e.g. engineered molecules for specific applications) and integrated into the total energy-infrastructure.

In this section we will not evaluate the design of the next generation petroleum refineries. We will discuss some important technology development directions for petroleum refineries, with an emphasis on the challenges faced by the Californian refinery industry. We focus on the main development areas and the discussion, almost by definition, is not exhaustive. The discussion below is guidance for the roadmap process, and does not intend to prescribe any selection or menu of technologies. This section aims to help the roadmap-process for technology development needs for the California Industries of the

Future and other R&D programs by providing input to the process by the industry and California Energy Commission as well as other participants.

5.2 Process Control

Energy management comprises a large variety of measures such as recognizing the importance of energy management, planning, monitoring, and implementing optimal control strategies. Generally, no or low initial costs are involved with these measures. We focus on process monitoring and energy management technologies. It is stressed that training and motivation are important, if not essential, measures in energy management, and should be an integral part of industrial energy management, as well as introduction of new technologies. A variety of process control systems are available for virtually any industrial process. A wide body of literature is available assessing control systems in most industrial sectors such as chemicals and petroleum refining. Table 6 provides an overview of classes of process control systems.

Table 6. Classification of Control Systems and Typical Energy Efficiency Improvement Potentials.

System	Characteristics	Typical energy savings (%)
Monitoring and Targeting	Dedicated systems for various industries, well established in various countries and sectors	Typical savings 4-17%, average 8% , based on experiences in the UK
Computer Integrated Manufacturing (CIM)	Improvement of overall economics of process, e.g. stocks, productivity and energy	> 2%
Process control	Moisture, oxygen and temperature control, air flow control "Knowledge based, fuzzy logic"	Typically 2-18% savings

Note: The estimated savings may be valid for specific applications (e.g. lighting energy use). The energy savings can not be added, due to overlap of the systems. Sources: (Caffal 1995, Martin et al., 2000).

Modern control systems are often not solely designed for energy efficiency, but rather at improving productivity, product quality and efficiency of a production line. Applications of advanced control and energy management systems are in varying development stages and can be found in all industrial sectors. Control systems result in reduced downtime, reduced maintenance costs, reduced processing time, and increased resource and energy efficiency, as well as improved emissions control (CADDET 1997). Many modern energy-efficient technologies depend heavily on precise control of process variables, e.g. strip casting in the steel industry and process integration in the chemical industries. Hence, in estimating the potential energy savings double counting should be avoided. Applications of process control systems are growing rapidly, and modern process control systems exist for virtually any industrial process. Still, large potentials exist to implement control systems, and more modern systems enter the market continuously. For example, the journal *Hydrocarbon Processing* produces a semi-annual overview of new advanced process control technologies for the oil refining industry (see e.g. HCP, 2001).

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Different control systems can also be integrated to optimize the operation of a process. Timmons et al (2000) report on the advantages of combining a online optimizer with an existing control system to optimize the operation of a FCC unit at the CITGO refinery in Corpus Christi, Texas. They report additional benefits of the online optimizer resulting in savings of $0.05/barrel at an "attractive" payback. Taylor et al. (2000) report on the application of two similar systems at a hydrotreater at a Sasol refinery in South Africa. By integrating the process controls of three reactors and a stripper they find increased yield (between 0.5 and 2.4% for diesel and gasoline respectively) and reduced hydrogen use and fuel use in the furnace and reboilers. The payback was less than two months.

Process control systems depend on information of many stages of the processes. A separate but important area is the development of sensors that are inexpensive to install, reliable, and analyze in real-time. Development aims at the use of optical, ultrasonic, acoustic, and microwave systems, that should be resistant to aggressive environments (e.g. oxidizing environments in furnace or chemicals in chemical processes) and withstand high temperatures. The information of the sensors is used in control systems to adapt the process conditions, based on mathematical ("rule"-based) or neural networks and "fuzzy logic" models of the industrial process.

Neural network-based control systems have successfully been used in the cement (kilns), food (baking), non-ferrous metals (alumina, zinc), pulp and paper (paper stock, lime kiln), petroleum refineries (process, site), and steel industries (EAFs, rolling mills). New energy management systems that use artificial intelligence, fuzzy logic (neural network), or rule-based systems mimic the "best" controller, using monitoring data and learning from previous experiences.

Process knowledge based systems (KBS) have been used in design and diagnostics, but are hardly used in industrial processes. KBS incorporates scientific and process information applying a reasoning process and rules in the management strategy. A recent demonstration project in a sugar beet mill in the UK using model based predictive control system demonstrated a 1.2 percent reduction in energy costs, while increasing product yield by almost 1 percent and reducing off-spec product from 11 percent to 4 percent. This system had a simple payback period of 1.4 years (CADDET, 2000). We did not find data on applications and energy savings achieved by KBS in the petroleum refining industry.

Although, energy management systems are already widely disseminated in various industrial sectors, the performance of the systems can still be improved, reducing costs and increasing energy savings further. For example, total site energy monitoring and management systems (Kawano 1996) can increase the exchange of energy streams between plants on one site. Traditionally, only one plant or a limited number of energy streams were monitored and managed. Various suppliers provide site-utility control systems (HCP, 2001).

Research for advanced sensors and controls is ongoing in all sectors, both funded with public funds as private research. Several projects within DOE's Industries of the Future try to develop more advanced control technologies (US DOE-OIT, 2000). Sensors and control techniques are identified as key technologies in various development areas including energy efficiency, mild processing technology, environmental performance and inspection and containment boundary integrity. Sensors and controls are also represented in a crosscutting OIT-program. Outside the U.S., Japan and Europe also give much attention to advanced controls. Future steps include further development of new sensors and control systems, demonstration in commercial scale, as well as dissemination of the benefits of control systems in a wide variety of industrial applications.

Due to the leadership of the Californian petroleum industry in product mix and processing, as well as environmental performance the state's industry is faced with major challenges before the rest of the country. Hence, improved process controls for combustion processes and product quality are areas of importance to the state's refining industry and state efforts in technology development.

5.3 Process Optimization and Integration

Process integration or pinch technology refers to the exploitation of potential synergies that are inherent in any system that consists of multiple components working together. In plants that have multiple heating and cooling demands, the use of process integration techniques may significantly improve efficiencies.

Developed in the early 1970's it is now an established methodology for continuous processes (Linnhoff, 1992; Caddet, 1993). The methodology involves the linking of hot and cold streams in a process in a thermodynamic optimal way (i.e. not over the so-called 'pinch'). Process integration is the art of ensuring that the components are well suited and matched in terms of size, function and capability. Pinch Analysis takes a systematic approach to identifying and correcting the performance limiting constraint (or pinch) in any manufacturing process (Kumana, 2000a). It was developed originally in the late 1970s at the University of Manchester in England and other places (Linnhoff, 1993) in response to the "energy crisis" of the 1970s and the need to reduce steam and fuel consumption in oil refineries and chemical plants by optimizing the design of heat exchanger networks. Since then, the pinch approach has been extended to resource conservation in general, whether the resource is capital, time, labor, electrical power, water or a specific chemical species such as hydrogen.

The critical innovation in applying pinch analysis was the development of "composite curves" for heating and cooling, which represent the overall thermal energy demand and availability profiles for the process as a whole. When these two curves are drawn on a temperature-enthalpy graph, they reveal the location of the process pinch (the point of closest temperature approach), and the minimum thermodynamic heating and cooling requirements. These are called the energy targets. The methodology involves first identifying the targets and then following a systematic procedure for designing heat exchanger networks to achieve these targets. The optimum approach temperature at the pinch is determined by balancing the capital-energy tradeoffs to achieve the desired

payback. The procedure applies equally well to new designs as well as retrofit of existing plants.

The analytical approach to this analysis has been well documented in the literature (Kumana, 2000b; Smith, 1995; Shenoy, 1994). Energy savings potential using Pinch Analysis far exceeds that from well-known conventional techniques such as heat recovery from boiler flue gas, insulation and steam trap management.

Pinch analysis, and competing process integration tools, have been developed further in the past years. The most important developments in the energy area are the inclusion of alternative heat recovery processes such as heat pumps and heat transformers, as well as the development of pinch analysis for batch processes (or in other words bringing in time as a factor in the analysis of heat integration). Furthermore, pinch analysis should be used in the design of new processes and plants, as process integration goes beyond optimization of heat exchanger networks (Hallale, 2001). Even in new designs often additional opportunities for energy-efficiency improvement can be identified. The pinch analysis has also been extended to the areas of water recovery and efficiency, and hydrogen recovery (Hydrogen Pinch, see also below). Water used to be seen as a low-cost resource to the refinery, and was used inefficiently. However, as the standards and costs for waste water treatment increase, as the costs for feedwater makeup increase, the industry has become more aware of water costs. In addition, large amounts of energy are used to process and move water through the refinery. Hence, water savings will lead to additional energy savings. Water Pinch can be used to develop targets for minimal water use by reusing water in an efficient manner. Optimization software has been developed to optimize investment and operation costs for water systems in a plant (Hallale, 2001). New tools have been developed to optimize water and energy use in an integrated manner (Wu, 2000). Water Pinch has until now mainly been used in the food industry, reporting reductions in water intake of up to 50% (Polley and Polley, 2000). We did not identify any Water Pinch analysis specific for the petroleum refining industry. Major oil companies, e.g. BP and Exxon, have applied Hydrogen Pinch analysis for selected refineries.

Process integration analysis of existing refineries and processes should be performed regularly, as continuous changes in product mix, mass flows and applied processes can provide new or improved opportunities for energy and resource efficiency.

Process integration remains an important area for development of analytical tools, as well as application to the environment of petroleum refineries.

5.4 Energy Recovery
At various stages in the refining process useful energy carriers may be lost. The most important (energy) sources are the recovery of combustible products for useful applications, which would have been flared otherwise, as well as the recovery of hydrogen from different flue and process gas streams. The latter will reduce the need for additional hydrogen makeup; an energy-intensive and expensive process.

Flare gas recovery (or zero flaring) is a strategy evolving from the need to improve environmental performance. Generally, conventional flaring practice has been to operate at some flow greater than the manufacturer's minimum flow rate to avoid damage to the flare (Miles, 2001). Typically, flared gas consists of background flaring (including planned intermittent and planned continuous flaring) and upset-blowdown flaring. In offshore flaring background flaring can be as much as 50% of all flared gases (Miles, 2001). In refineries, background flaring will generally be less than 50%, depending on practices in the individual refinery. Recent discussions on emissions from flaring from Bay Area refineries has highlighted the issue from an environmental perspective (Ezerksy, 2002).[6] The report highlighted the higher emissions compared to previous assumptions of the Air Quality district, due to larger volumes of flared gases. The report also demonstrated the differences among various refineries, and plants within the refineries. Reduction of flaring will not only result in reduced air pollutant emissions, but also in increased energy-efficiency replacing fuels, as well as less negative publicity around flaring.

Reduction of flaring can be achieved by improved recovery systems, including installing recovery compressors and collection and storage tanks. This technology is commercially available. For example, an Arkansas refinery recently installed a new flare gas recovery system to reduce emissions. New compressors and liquid-seals have been installed, and the two flare gas recovery systems have reduced flaring to near-zero levels (Fisher and Brennan, 2002). A plant-wide assessment of the Equilon refinery in Martinez (now fully owned by Shell) highlighted the potential for flare gas recovery. The refinery will install new recovery compressors and storage tanks to reduce flaring. No specific costs were available for the flare gas recovery project, as it is part of a large package of measures for the refinery. The overall project has projected annual savings of $52 Million and a payback period of 2 years (US DOE-OIT, 2002).

However, emissions can be further reduced by improved process control equipment and new flaring technology. Development of gas-recovery systems, development of new ignition systems with low-pilot-gas consumption or elimination of pilots altogether with the use of new ballistic ignition systems can reduce the amount of flared gas considerably. Development and demonstration of new ignition systems without a pilot may result in increased energy efficiency and reduced emissions.

Hydrogen Management and Recovery. Hydrogen is used in the refinery in processes such as hydrocrackers and desulfurization using hydrotreaters. The production of hydrogen is an energy intensive process using natural gas-fueled reformers. However, these processes and other processes generate gases that may contain a certain amount of hydrogen not used in the processes, or generated as by-product of distillation of conversion processes. In addition, different processes have varying quality (purity) demands for the hydrogen feed. Reducing the need for hydrogen make-up will reduce energy use in the reformer and reduce the need for purchased natural gas. Natural gas is

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[6] ChevronTexaco commented on the report by the Bay Area Air Quality Management District on refinery flaring. The comments were mainly directed towards the VOC-calculations in the report and an explanation of the flaring practices at the ChevronTexaco refinery in Richmond, CA (Hartwig, 2003).

an expensive energy input in the refinery process, and lately associated with large fluctuation in prices (especially in California). The major technology developments in the hydrogen management within the refinery are hydrogen process integration (or hydrogen cascading) and hydrogen recovery technology (Zagoria and Huycke, 2003). Revamping and retrofitting existing hydrogen networks can increase hydrogen capacity between 3% and 30% (Ratan and Vales, 2002).

Hydrogen integration at refineries is a new and important application of pinch analysis (see above). Most hydrogen systems in refineries feature limited integration and pure hydrogen flows are sent from the reformers to the different processes in the refinery. But as the use of hydrogen is increasing, especially in Californian refineries, the value hydrogen is more and more appreciated. Using the approach of composition curves used in pinch analysis the production and uses of hydrogen of a refinery can be made visible. This allows to identify the best matches between different hydrogen sources and uses based on quality of the hydrogen streams. It allows the user to select the appropriate and most cost-effective technology for hydrogen purification. A recent improvement of the analysis technology also accounts for gas pressure, to reduce compression energy needs (Hallale, 2001). The analysis method accounts also for costs of piping, besides the costs for generation, fuel use and compression power needs. It can be used for new and retrofit studies.

The BP refinery at Carson, in a project with the California Energy Commission, has executed a Hydrogen Pinch analysis of the large refinery. Total potential savings of $4.5 Million on operating costs were identified, but the refinery decided to realize a more cost-effective package saving $3.9 Million per year. As part of the plant-wide assessment of the Equilon (Shell) refinery at Martinez an analysis of the hydrogen network has been included (US DOE-OIT, 2002). This has resulted in the identification of large energy savings. Further development and application of the analysis method at Californian refineries, especially as the need for hydrogen is increasing due to reduced future sulfur-content of diesel and other fuels, may result in reduced energy needs at all refineries with hydrogen needs (all, except San Joaquin Refining in Bakersfield) (Khorram and Swaty, 2002). One refinery identified savings of $6 Million/year in hydrogen savings without capital projects (Zagoria and Huycke, 2003).

Hydrogen recovery is an important technology development area to improve the efficiency of hydrogen recovery, reduce the costs of hydrogen recovery and increase the purity of the resulting hydrogen flow. Hydrogen can be recovered indirectly by routing low-purity hydrogen streams to the hydrogen plant (Zagoria and Huycke, 2003) or can hydrogen can be recovered from offgases by routing it to the existing purifier of the hydrogen plant, or by installing additional purifiers to treat the offgases and ventgases. The cost savings of recovered hydrogen are around 50% of the costs of hydrogen production (Zagoria and Huycke, 2003). Membranes are an attractive technology for hydrogen recovery. If the content of recoverable products is higher than 2-5% (or preferably 10%) recovery may make economically sense (Baker et al., 2000). New membrane applications for the refinery and chemical industry are under development. Membranes for hydrogen recovery from ammonia plants have first been demonstrated

about 20 years ago (Baker et al., 2000), and are used in various state-of-the-art plant designs. Refinery offgas flows have a different composition, making different membranes necessary for optimal recovery. Membrane plants have been demonstrated for recovery of hydrogen from hydrocracker offgases. Various suppliers offer membrane technologies for hydrogen recovery in the refining industry, including Air Liquide, Air Products and UOP. The hydrogen content has to be at least 25% for economic recovery of the hydrogen, with a recovery yield of 85-95% and a purity of 95%.

Membrane technology generally represents the lowest cost option for low product rates, but not necessarily for high flow rates (Zagoria and Hucyke, 2003). For high-flow rates PSA technology is often the conventional technology of choice. Development of low-cost and efficient membranes is an area of research interest to improve cost-effectiveness of hydrogen recovery, and enable the recovery of hydrogen from gas streams with lower concentrations.

Heat Recovery. Heat is recovered and re-used throughout the refinery. Next to efficient integration of heat flows throughout the refinery (see process integration above), the efficient operation of heat exchangers is a major area of interest. In a complex refinery most processes occur under high temperature and pressure conditions; the management and optimization of heat transfer among processes is therefore key to increasing overall energy efficiency. Fouling, a deposit buildup in units and piping that impede heat transfer, requires the combustion of additional fuel. For example, the processing of many heavy crude oils in the U.S. increases the likelihood of localized coke deposits in the heating furnaces, thereby reducing furnace efficiency and creating potential equipment failure. An estimate by the Office of Industrial Technology at the U.S. Department of Energy noted that the cost penalty for fouling could be as much as $2 billion annually in material and energy costs. The problem of fouling is expected to increase with the trend towards processing heavier crudes.

Fouling is the effect of several process variables and heat exchanger design. Fouling may follow the combination of different mechanisms (Bott, 2001). Several methods of investigation have been underway to attempt to reduce fouling including the use of sensors to detect early fouling, physical and chemical methods to create high temperature coatings (without equipment modification), the use of ultrasound, as well as the improved long term design and operation of facilities. The U.S. Department of Energy initially funded preliminary research into this area, but funding has been discontinued (Huangfu, 2000; Bott, 2000).

Initial analysis on fouling effects of a 100,000 bbl/day crude distillation unit found an additional heating load of 12.3 kBtu/barrel (13.0 MJ/barrel) processes (Panchal and Huangfu, 2000). Reducing this additional heating load could results in significant energy savings.

This technology is still in the conceptual and basic research stage and therefore it is difficult to assess capital costs at this time. Argonne National Laboratory (ANL) has been the lead in working with the refining industry in the area. Progress so far has included: a

basic understanding of fouling mechanisms developed (for example, the presence of iron sulfide in crude oil and its link to fouling), the development of a threshold fouling model by ANL, the testing of prototype fouling detection units, the development of a Heat Exchanger Design Handbook (1999 Edition) incorporated ANL's petroleum fouling threshold model, and the preparation of a guideline document on Heat Exchanger Fouling in the Crude Oil Distillation Unit (Panchal, 2000). Besides ANL several other groups have worked in the area of fouling reduction. Outside the U.S. different groups in Europe and Canada have worked on fouling.

While the issue of fouling is now on the radar screen of plant managers (there is a bi-annual Fouling Mitigation conference held by the American Institute for Chemical Engineers), a stronger commitment by the refining industry would be needed to advance this technology to the next stage of development. Some sources believe that the future development of in this area is expected to be in the area of Condition-Based Maintenance of Heat-Transfer Equipment that will be based on Knowledge-Based and Monitoring - Based Mitigation of Fouling/Corrosion (Panchal, 2000), see also section on process control systems). Furthermore, developments in heat exchanger design and process intensification may also contribute to reducing the problem of fouling.

5.5 Catalysts
Catalysts are key to the conversion and processing efficiency of all conversion processes in the refinery. The main refining processes using catalysts are hydrotreating, FCC, reforming, hydrocracking, alkylation and isomerization. New catalysts can improve the efficiency of these processes by increasing the conversion rate of a chemical reaction, increasing the selectivity of chemical reactions (i.e. reducing the speed of side-reactions), or improving the reaction conditions (e.g. lower pressure or temperatures). Catalyst development is hence an important element in defining the future efficiency of refining processes and the design of these processes.

Many scientific groups around the world are active in catalyst research and development, while a number (26 in 2001) of major catalyst suppliers operate worldwide to supply and recycle catalysts. The market for catalysts will grow, especially due to lower sulfur content of fuels (Prada Silvy, 2002). Finding new in catalyst is much like a trial-and-error process, although recent progress in the combinatorial development programs have led to increased development rates of new catalysts. Nevertheless, many new interesting developments in catalysts for petroleum refining are underway.

The major new developments are expected in the development of *hydrotreater* catalysts. Hydrotreaters are the major catalyst user in the refining industry (approximately 34% of the global refining catalyst market). The major directions for improvement of hydrotreater catalysts are higher activity, longer life, reduced costs and optimized process conditions. The major R&D areas are new metallic catalysts for deep hydrogenation, new and tailor-made catalyst supports, and multi-bed reactors (Prada Silvy, 2002; Babich and Moulijn, 2003).

FCC catalyst development (30% of the market) aims at the use of heavier feedstocks, reduced sulfur content in gasoline (Prada Silvy, 2002; Genco et al., 2001), longer lifetime (Patrie et al., 2001), controlled selectivity, and increased yields. Major R&D areas are reduced FCC contact time, new catalysts additives and development of new zeolite catalysts (Prada Silvy, 2002).

In *reforming* (6% of global catalyst market) the major challenges are new trimetallic catalysts systems that increase yields, improve selectivity and stability at low pressures, as well increased lifetime (Prada Silvy, 2002).

In *hydrocracking* (5% of current refining catalyst market, but strongly increasing) the major new developments include increased middle distillate yield, lower hydrogen consumption and pressure, and higher resistance to coke deactivation. The major R&D area are bifunctional metal-acid catalyst systems.

In *alkylation* the main trend is to develop alternative catalysts to replace the HF and sulfuric acid catalysts currently in use. The future trend for alkylation catalysts are solid super-acid catalysts based on zeolites or other amorphous acidic silica alumina catalysts (Prada Silvy, 2002). In *isomerization* the main research trend aims at the development of new superacid solid catalysts to improve the performance at lower temperatures.

5.6 Reactor Design
While new processes are developed by many of the suppliers to the oil industry, most of these represent slight changes to previous designs, improving productivity, energy efficiency and lowering production costs. However, from an R&D perspective there are also important new approaches to reactor design. Below we will discuss some of the interesting new developments in process and reactor design in the petroleum refining industry.

One of the most promising pathways to simultaneously reduce energy use and capital costs is **process intensification**. Process Intensification is a new area of reactor development aiming at more compact reactors to dramtacially reduce the size of chemical plants, reduce capital costs and intensify the chemical reactions (Stankiewicz and Moulijn, 2000). Process intensification started in the early 1990's and was taken up by the British energy agencies as potential approach to improve energy efficiency. Process intensification aims at the design of new compact reactors, and on the combination and integration of different processes (e.g. conversion and separation). The former has given rise to the development of compact heat exchangers that work under more extreme conditions (see e.g. Haslego, 2001). An example of the latter is the design by Sulzer and an European consortium to integrate the chemical conversion with a distillation column (Moritz and Gorak, 2002). An example of process intensification in the refinery industry is reactive distillation.

In **distillation** the main shot-term developments are in improved integration through the use of heat recovery technology and integration of different distillation units (i.e. CDU and VDU). On the long-term the major developments are the integration of different

distillation columns into one reactor (e.g. dividing-wall column) or the development of alternative processing routes allowing for combination of conversion and distillation (e.g. reactive distillation). Alternatives to distillation may also include membranes (Dorgan et al., 2003). Other alternatives for distillation include technologies such as freeze concentration. However, freeze concentration's costs seems to limit this technology to specialized applications in the chemical and food industries.

Improved integration of heat pumps and transformers may allow increased recovery of products, leading to net energy savings. Heat pumps are found in the chemical industry for specific (large scale) applications (e.g. styrene/propylene oxide production), but have not entered the refinery industry. Petrick and Pellegrino (1999) describe the application of an absorption refrigeration unit, using waste heat, to recover additional LPG from a reformer reactor. The installation at a refinery in Denver, Colorado had a payback period of 1.5 years. The amount of additional recovered LPG depends on the ambient temperature, as the losses are higher during the summer. Petrick and Pellegrino (1999) also report on using similar technology for the CDU estimating energy savings of over 17%. With an estimated payback period of 1-2 years. The authors are not aware of any applications of this technology for a CDU.

Dividing-Wall Distillation. The concept of dividing-wall columns originates from 1949, but it was not until recently that practical and commercial designs became possible. Process integration studies and other development work since the early 1990's have resulted in the first commercial application of the dividing-wall distillation column (Hallale, 2001). A dividing-wall column integrates two conventional distillation columns into one column increasing heat transfer. Dividing-wall columns (DWC) can save up to 30% in energy costs, while providing lower capital costs, compared to conventional columns (Schultz et al., 2002). Various companies (Kellog Brown & Root, Krupp Uhde, Linde, Sumitomo, and UOP) have developed DWC-concepts for the separation of products. BASF in Germany pioneered the DWC and operates the largest number of DWCs in the world in their chemical plants. In petroleum refining BP, Veba Oel (Germany), Sasol (South Africa) and Chevron operate DWCs. Current DWC-applications are limited to benzene removal from gasoline or the separation of lighter fractions in gasoline production. Further development of DWC for the major distillation processes in the petroleum refining industry is necessary.

Membranes may offer future alternatives to distillation. Membranes have started to enter the refinery for hydrogen recovery (see above), but are also being developed for other separations. An extensive study funded by DOE focused on membranes for different separations (gas/gas, fluid/fluid) and studied current state-of-the-art and the potential applications in petroleum refining (Dorgan et al., 2003). The report concludes that membrane technology will definitely enter the refinery, although further research is needed to develop appropriate membrane materials that can withstand the environment found in petroleum refining processes. Also, membrane technology should be evaluated as an integrated part of the specific process for which it's being implemented to warrant the full energy savings potential.

Conversion Processes. The major new development area for conversion processes will be the combination of conversion and separation, i.e. *reactive distillation*. By combining the chemical reaction and separation in one reactor capital costs are reduced, and energy efficiency is improved through better integration of these process steps. Reactive distillation offers a promising alternative to conventional reaction-distillation schemes (Sundmacher and Kienle, 2003). Furthermore, active removal of reaction products can help shift the equilibrium of the reaction and improve the conversion efficiency. Reactive distillation has mainly be used in acetate technology (e.g. MTBE production) (Moritz and Gorak, 2002). Various research institutes and technology developers aim at developing new applications of reactive distillation. In the U.S. a study developed a reactive distillation process for isomerization to produce clean high-octane isomerate (US DOE-OIT, 2001). In Europe, a collaborative project of suppliers and universities aims to improve understanding of reactive distillation and develop simulation tools to design new applications. Other new developments include the use of monolithic structures that contain the catalysts (Babbich and Moulijn, 2003) reducing catalyst loss (Goetze and Bailer, 1999). Monolithic structures result in low pressure drop.

In the Fluid Catalytic Cracker (FCCU) the major developments are in the integration with sulfur removal to produce low-sulfur gasoline without octane loss (Babbich and Moulijn, 2003). This development will build on the development of new catalysts (see above). New catalysts will contribute to improved yields and improved selectivity. Furthermore, power recovery turbines can be installed on FCC units to produce power of the pressure of the offgases of the FCC. This technology is commercially proven, but currently used in only a few refineries in California (e.g. BP/ARCO in Los Angeles).

Various authors have proposed to by-pass the CDU/VDU by directly feeding crude oil to a thermal cracking process (Petrick and Pellegrino, 1999). The cracking process would provide sufficient flexibility to supply a varying need of products. The authors have not studied the impact of such schemes on energy consumption. However, Petrick and Pellegrino estimate net energy savings from such a scheme, based on a simplified model of the process and the traditional distillation process route.

Desulfurization/Hydrotreater. With the increased focus to reducing sulfur content in fuels, the role of desulfurization in the refinery becomes more and more important. Currently, the process of choice is the hydrotreater, in which hydrogen is added to the fuel to remove the sulfur from the fuel. Some hydrogen may be lost to reduce the octane number of the fuel, which is undesirable. Because of the increased attention for fuel desulfurization various new process-concepts are being developed with various claims of efficiency and effectiveness. Babich and Moulijn (2003) provide an overview of the major new developments in desulfurization. The three main routes are advanced hydrotreating (new catalysts, catalytic distillation, processing at mild conditions), reactive adsorption (type of adsorbent used, process design) and oxidative desulfurization (catalyst, process design). Several of these concepts are now being demonstrated at refiniries around the world. An advanced hydrotreating process has been developed by a CDTech Company and demonstrated at refineries at Port Arthur (Texas) (Babbich and Moulijn, 2003) and Saint John (New Brunswick) (Gardner et al., 2001). Philips

Petroleum developed an absorbent process (S Zorb) which is being demonstrated at the Borger (Texas) refinery (Gislason, 2001), while Biodesulfurization may potentially be viable for specific refinery streams.

Other Refinery Processes. New developments for other process concentrate on the integration of various process steps (reactive distillation), new catalysts and new reactor designs.

5.7 Biotechnology

Biotechnology is actively considered by the refining industry as an alternative to some of the current processes. A collaboration between Shell and the Rocky Mountains Institute is looking at innovative ways to reduce the CO_2 emissions of a refinery to net zero emissions through the use of biotechnology and biomass as an alternative feedstock (other then ethanol from corn). Biodesulfurization has received attention from two DOE-funded projects.

Biodesulfurization is an alternative to the current hydrotreater. While other alternatives to hydrotreaters are under development to desulfurize various refinery products, biodesulfurization would be a complete breakthrough in process development. It would offer mild processing conditions and reduce the need for hydrogen makeup. Both would lead to high energy savings in the refinery. Biocatalytic desulfurization (BDS) can potentially offer a low-cost alternative to hydrotreating, reducing capital and operating costs (US DOE-OIT, 2003). A previous study has developed a design for the process and evaluated the economics (Enchira, 2003). The challenge is to develop bacteria that can reduce the sulfur content of gasoline to a sufficiently low level to meet fuel standards at sufficiently high rate of desulfurization (Borole et al., 2003). Other challenges include biocatalyst stability, oil-water separation and product recovery (Borole et al., 2003).

5.8 Combustion Technology

Combustion is key in many of the processes used in the refinery. Boilers, furnaces and process heaters all apply burners to efficiently generate heat to produce steam, electricity and heat. Burner development is challenged by many issues. Foremost are challenges to reduce emissions from burners (i.e. NOx, CO, PM), as well as to increase the heat transfer and combustion efficiency of the burner. Other challenges include fuel flexibility, robust operating controls, improved safety, reliability and maintenance and lower costs (US DOE-OIT, 2002b). Small changes in the efficiency of combustion systems may provide large energy cost savings. Also, the use of low-NOx burners may result in indirect capital and energy savings, as it avoid the use of selective catalytic reduction. Hence, combustion technology is still an important R&D area with potential for new technologies.

US DOE has produced a roadmap for the combustion industry outlining the major challenges and R&D directions for burners in boilers and furnaces (US DOE-OIT, 2002b). New burner designs aim at improved mixing of fuel and air and more efficient heat transfer. Many different concepts are developed to achieve these goals, including lean-premix burners (Seebold et al., 2001), swirl burners (Cheng, XXXX), pulsating

burners (Petrick and Pellegrino, 1999) and rotary burners (US DOE-OIT, 2002c). It is impossible to outline all potential burner developments in this report, and hence we refer to roadmap.

5.9 Utilities
Although utilities represent only a small part of the energy consumption at refineries, energy savings are possible. New technology development in pumping (e.g. dry vacuum pumps), power technology (e.g. adjustable speed rives and power electronics) and compressors can result in direct energy savings. The relative high power costs in California make these new technologies attractive. Also, new waste water treatment technology may help reduce the effluent quantity and improve the quality. New technologies like reverse osmosis (RO) and other membrane technology may soon enter the refinery as well. RO has been used widely in the food industries to upgrade feedwater and also treat waste water.

5.10 Power Generation
The petroleum refining industry is one of the largest users of cogeneration or CHP in the country. The petroleum refining industry is also identified as one of the industries with the largest potential for increased application of CHP. We estimate installed CHP capacity in Californian refineries at at least 1400 MWe.

Where process heat, steam or cooling and electricity are used, cogeneration plants are significantly more efficient than standard power plants because they take advantage of what are losses in standard plants by utilizing waste heat. In addition, transportation losses are minimized when CHP systems are located at or near the refinery. Utility companies have been developing CHP for use by refineries. In this scenario, the utility company owns and operates the system for the refinery, which avoids the capital expenditures associated with CHP projects, but gains the benefits of a more energy efficient system of heat and electricity. For systems requiring cooling, absorption cooling can be combined with CHP to use waste heat to produce cooling power.

Innovative gas turbine technologies can make CHP more attractive for sites with large variations in heat demand. *Steam injected gas turbines* (STIG, or Cheng cycle) can absorb excess steam, e.g. due to seasonal reduced heating needs, to boost power production by injecting the steam in the turbine. The size of typical STIGs starts around 5 MWe. STIGs are found in various industries and applications, especially in Japan and Europe, as well as in the U.S. Energy savings and payback period will depend on the local circumstances (e.g. energy patterns, power sales conditions).

High-temperature turbines can be pre-coupled to a crude distillation unit (or other continuously operated processes with an applicable temperature range). The offgases of the gas turbine can be used to supply the heat for the distillation furnace, if the outlet temperature of the turbine is high enough. One option is the so-called `repowering' option. In this option, the furnace is not modified, but the combustion air fans in the furnace are replaced by a gas turbine. The exhaust gases still contain a considerable amount of oxygen, and can thus be used as a combustion air for the furnaces. The gas

turbine can deliver up to 20% of the furnace heat. Two of these installations are installed in the Netherlands, with a total capacity of 35 MW_e at refineries (Worrell et al., 1997).

Another option, with a larger CHP potential and associated energy savings, is `high-temperature CHP'. In this case, the total heat demand of the furnace is delivered by a CHP plant. This option requires replacing the existing furnaces. This is due to the fact that the radiative heat transfer from gas turbine exhaust gases is much smaller than from combustion gases, due to their lower temperature (Worrell et al., 1997). A distinction is made between two different types. In the first type, the exhaust heat of a gas turbine is led to a `waste heat recovery furnace', in which the process feed is heated. In the second type the exhaust heat is led to a `waste heat oil heater' in which thermal oil is heated. By means of a heat exchanger, the heat content is transferred to the process feed. In both systems, the remaining heat in the exhaust gases after heating the process feed should be used for lower temperature purposes to achieve a high overall efficiency. The second type is more reliable, due to the fact that a thermal oil buffer can be included. The main difference is that in the first type the process feed is directly heated by exhaust gases, where the second uses thermal oil as an intermediate, leading to larger flexibility. An installation of the first type is installed in Fredericia, Denmark at a Shell refinery. The low temperature remaining heat is used for district heating. R&D has to be aimed at making detailed design studies for specific refineries and the optimization of furnace design, and more demonstration projects have to be carried out.

Gasification. Because of the increased demand for lighter products and increased use of conversion processes, refineries will have to manage an increasing stream of heavy bottoms and residues. Gasification of the heavy fractions and coke to produce synthesis gas can help to efficiently remove these by-products. The state-of-the-art gasification processes combine the heavy by-products with oxygen at high temperature in an entrained bed gasifier. Due to the limited oxygen supply, the heavy fractions are gasified to a mixture of carbon monoxide and hydrogen. Sulfur can easily be removed in the form of H2St produce elemental sulfur. The synthesis gas can be used as feedstock for chemical processes. However, the most attractive application seems to be generation of power in an Integrated Gasifier Combined Cycle (IGCC). In this installation the synthesis gas is combusted in a gas turbine (with an adapted combustion chamber to handle the low to medium-BTU gas) generating electricity. The hot fluegases are used to generate steam. The steam can be used onsite or used in a steamturbine to produced additional electricity (i.e. the combined cycle).

Entrained bed IGCC technology is originally developed for refinery applications, but is also used for the gasification of coal. Hence, the major gasification technology developers were oil companies like Shell and Texaco. IGCC is used by the Shell refinery in Pernis (The Netherlands) to treat residues from the hydrocracker and other residues to generate 110 MWe of power and 285 tonnes of hydrogen for the refinery. Also, the IPA Falconara refinery (Italy) uses IGCC to treat visbreaker residue to produce 241 MWe of power (Cabooter, 2001). New installations have been announced or are under construction for the Sannazzaro refinery (Agip, Italy), Lake Charles, (Citgo, Louisiana) and Bulwer Island (BP, Australia).

IGCC provides a low-cost opportunity to reduce emissions (SOx, NOx) when compared to combustion of the residue, and to process the heavy bottoms and residues while producing power and/or feedstocks for the refinery. IGCC provides an especially interesting alternative for Californian refineries due to the already high fraction of light products (and hence increased production of residue fractions), the high cost of power and stringent air pollution standards for most refinery locations in California.

6. Summary and Conclusions

Refineries are the largest energy using industry in California, and the most energy intensive industry in the United States. Petroleum refining industries have evolved from relatively simple distillation-based plants to highly complex and integrated distillation and conversion processes. In fact, the petroleum refining industry of today looks more like the chemical industry. Refineries are facing many challenges, e.g. increased fuel quality, heavier crudes and changing product mix, increasing and more volatile energy prices, need to reduce air pollutant emissions, increased pressure on profitability, as well as increased safety demands. These challenges will affect the industry and technology choice profoundly. In this report we have discussed the historical development of the petroleum refining industry in the U.S. and California. The analysis showed that the Californian refining industry is the leader in many of the identified challenges to the national industry. This report aims to provide background information for the development of a research and development roadmap for the Californian petroleum refining industry.

The U.S. petroleum processes almost 25% of the world's annual crude oil production. The U.S. petroleum refining industry consumes over 3.2 Quads of primary energy, mainly in the form of refinery by-products (e.g. refinery gas, coke), natural gas and electricity. California has the third largest refining industry in the nation, after Texas and Louisiana. The Californian petroleum industry represents approximately 12% of the nation's industry, expressed in crude intake capacity. In California 8 companies operate 14 refineries, with concentrations in the San Francisco Bay area and Los Angeles. The industry in California produces a distinctly different mix of products when compared to the nation's average, which is reflected in the increased demand for lighter products (e.g. gasoline) and cleaner products. This difference is reflected in the processes used by the industry in California, as well as in the energy intensity. There is no public data available on the total energy consumption of petroleum refineries in California. We estimate the primary energy consumption at 495 TBtu.

On the long-term the refinery of the future will be distinctly different from today's. In the report we outlined major technology development areas, and which are summarized in Table 7.

Table 7. Major technology development directions for the petroleum refining industry.

Technology Area	Technology Examples
Process Control	Neural networks, knowledge based systems
Process Optimization and Integration	Analytical tools, site integration
Energy Recovery	Hydrogen recovery and integration, flare gas recovery
Catalysts	Higher selectivity, increased lifetime
Reactor Design	Process intensification, membranes, reactive distillation, dividing-wall column
Biotechnology	Biodesulfurization, bio-feedtsocks
Combustion Technology	Low NOx burners, high-efficiency burners
Utilities	Membranes, low-maintenance pumps
Power Generation	Advanced cogeneration, Gasification (IGCC), power recovery

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